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TRANSACTIONS

OF THE

AMERICAN INSTITUTE

OF

CHEMICAL ENGINEERS

VOLUME XIV

1921-22

OFFICE OF THE SECRETARY
POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

PUBLISHED BY THE INSTITUTE
AND FOR SALE BY
D. VAN NOSTRAND COMPANY
NEW YORK
1923

660.6

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TRANSACTIONS OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

THERMAL CONSIDERATIONS IN SULPHURIC ACID CONCENTRATION

A Study of the Available Data on the Physical Properties of Sulphuric Acid Solutions from Which Are Derived Convenient Curves for Determining the Heat Required for Concentration.

By FRED C. ZEISBERG

Read at the Niagara Falls Can. Meeting, June 18, 1922.

Sulphuric acid is universally concentrated by the application of heat. The first interest of the designer of apparatus to concentrate sulphuric acid must hence lie in the thermal properties of sulphuric acid. Several articles have been written on this subject,[1] and one of them[2] at least has treated the subject very thoroughly and comprehensively. The results, however, are not most conveniently expressed, and the original article is not particularly accessible. This, then, must be the excuse for the present attempt to present an old subject from a different viewpoint.

Specific Heat

The first thermal property of sulphuric acid which interests us is its specific heat. Many determinations have been made[3] of this con-

[1] S. U. Pickering, *J. Chem. Soc.*, vol. 57, pp. 64–184; 331–369 (1890); R. Knietsch, *Ber.*, vol. 34, pp. 4069–4115 (1901); Norman Swindin, *Chem. Trade J.*, vol. 59, pp. 369–371 (1916); F. Colin Sutton, *Chem. Age (London)*, vol. 5, pp. 178–180 (1921); L. Cerutty, *Chem. Age (London)*, vol. 5, pp. 769–760 (1921).

[2] A. W. Porter, *Trans. Faraday Soc.*, vol. 13, pp. 373–400 (1918).

[3] Herman Schlesinger, *Physik. Z.*, vol. 10, pp. 210–215 (1909); C. de la Condamine, *Ind. Chim.*, vol. 5, pp. 153–155 (1918); Paul Pascal and Garnier, *Bull. Soc. Chim.*, vol. 27, pp. 8–17 (1920); R. Knietsch, *Ber.*, vol. 34, pp. 4069–4115 (1901).

stant, in addition to those given in Landolt-Börnstein. The figures of Knietsch are out of line with those of other workers, while those of Pascal [3] seem the most probably correct, and are shown graphically in Fig. 1 by the full line. It will be noted that these are for 20 deg. C. As the temperature rises the specific heat increases slightly, but no extensive investigation of the change at various concentrations seems

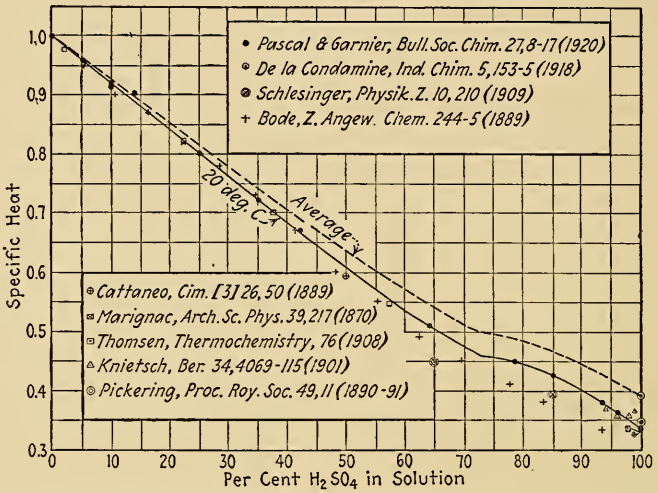


FIG. 1. Specific Heat of Sulphuric Acid Solutions at 20 Deg. C., and Average Specific Heat Between 20 Deg. C. and the Boiling Point

to have been made. Figures reported by de la Condamine [4] indicate that, if the increase of specific heat with the temperature is linear, the average specific heat of 100 per cent H_2SO_4 between 20 deg. C. and the boiling point is about 0.39. There has hence been drawn in Fig. 1 the dotted curve giving the probable value of the average specific heats between 20 deg. C. and the boiling point for all concentrations of H_2SO_4 solution. The values given by this dotted curve have been used in the calculations which follow.

Boiling Point

The next thermal property of sulphuric acid which interests us is the boiling point of various strength solutions. A number of investigators [5] have studied this property, but the results of Burt's work

[4] C. de la Condamine, *Ind. Chim.*, vol. 5, pp. 153–155 (1918).

[5] R. Knietsch, *Ber.*, vol. 34, pp. 4069–4115 (1901); G. Lunge and F. Salathe,

appear the most trustworthy. In Fig. 2 the various data have been plotted, the curve being drawn with respect mostly to the points obtained by Burt and Ferguson. Here, again, it will be observed that Knietsch's results are out of line with those of other investigators. Values read from the curve have been used in the calculations which follow.

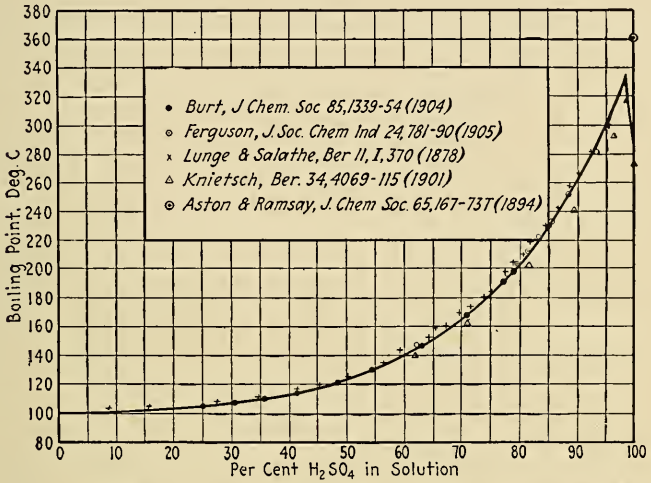


FIG. 2. Boiling Points of Sulphuric Acid Solutions at 760 Mm.

PARTIAL PRESSURES OF VAPORS FROM BOILING H_2SO_4

Another thermal property which interests us is the composition of the vapor emitted by boiling sulphuric acid solutions. The literature appears to contain no definite figures, but numerous indefinite references such as that "boiling sulphuric acid solutions give off nothing but water vapor until 170 deg. C., equivalent to 72 per cent H_2SO_4, is reached."[4] The du Pont company several years ago made some rough determinations of these partial pressures,[6] which are shown graphically in Fig. 3.

HEAT OF DILUTION

Still another thermal property which must be known is the heat of dilution of sulphuric acid. This has been investigated by a num-

Ber., vol. 11, No. 1, pp. 370–374 (1878); E. A. Aston and W. Ramsay, *J. Chem. Soc.*, vol. 65, pp. 167–173T (1894); B. C. Burt, *J. Chem. Soc.*, vol. 85, pp. 1339–1354 (1904); W. C. Ferguson, *J. Soc. Chem. Ind.*, vol 24, pp. 781–790 (1905).

[6] W. C. Sproesser, private communication in du Pont files.

ber of investigators,[7] the values obtained by Thomsen[8] having been selected for use herein. These values are shown graphically in Fig. 4,

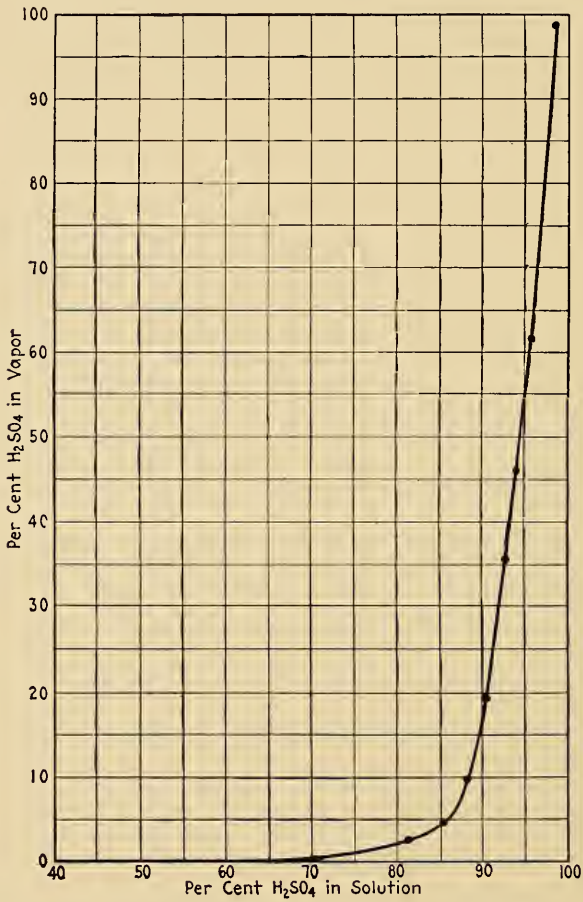


FIG. 3. Composition of Vapors in Equilibrium with Boiling Sulphuric Acid Solutions at 760 Mm.

where both the curve obtained from the experimental results (full) and the one obtained by using the formula derived by Thomsen (dotted) are shown. This formula, it will be observed, agrees well

[7] R. Knietsch, *Ber.*, vol. 34, pp. 4069–4115 (1901); L. Pfaundler, *Ber.*, vol. 3, pp. 798–800 (1870); J. N. Brönsted, *Z. Physik. Chem.*, vol. 68, pp. 693–725 (1910).

[8] J. Thomsen, "Thermochemistry," p. 78, 1908.

with the experimentally determined points from about 20 per cent H_2SO_4 to 100 per cent.

Heat of Vaporization

The final property which interests us is the heat of vaporization of water. As is well known, this varies with the temperature, and Fig. 5 shows this variation graphically between 0 deg. C. and 350 deg. C., the values of Marks and Davis[9] having been used. In some cases, also, the heat of vaporization of H_2SO_4 itself may be of interest. This is 220 B.t.u. per lb. 100 per cent H_2SO_4.

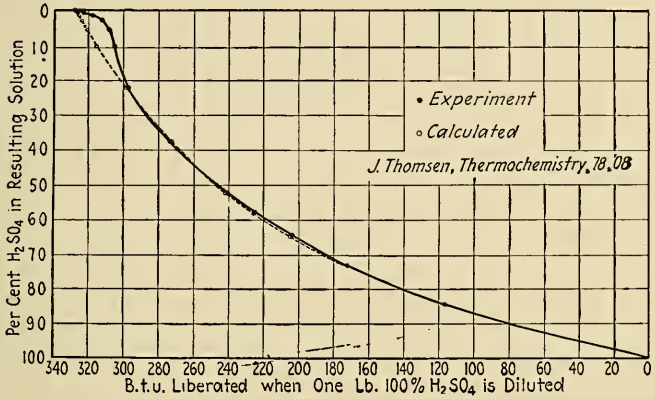


Fig. 4. Heat of Dilution of Sulphuric Acid

Thermal Considerations in Concentration

If we now make the assumption that, in the concentration of a given quantity of sulphuric acid solution, it can be heated to the boiling point without the evaporation of any water until the boiling point is reached, the heat input up to the boiling point is made up solely of the sensible heat, which can be expressed by the equation

$$H_s = ws(t_b - t) \qquad (1)$$

in which H_s = sensible heat in B.t.u.,
w = weight of acid in pounds,
s = specific heat of acid,
t_b = boiling point in deg. F.,
t = original temperature.

[9] Marks and Davis, "Steam Tables and Diagrams," 1909.

After the boiling point is reached, continued input of heat accomplishes three things: water is evaporated, hydrates of H_2SO_4 are decomposed, and the resulting more highly concentrated solution is raised to a new, higher boiling point. It is therefore perfectly proper

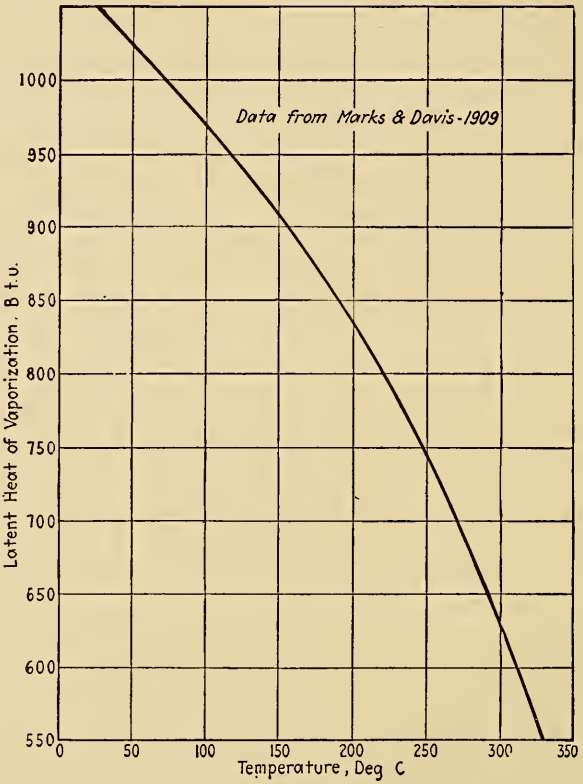


FIG. 5. Heat of Vaporization of Water

to regard the heat necessary after the boiling point has been reached as made up of three components, which, for convenience, can be called the heat of vaporization, H_v; the heat of dehydration, H_d; and the heat of maintained boiling, H_b.

The heat of vaporization is made up wholly, at the lower concentrations, of the heat of vaporization of water. At the higher concentrations there is added to it the heat of vaporization of the sulphuric acid carried along with the water—viz., 220 B.t.u. per lb. H_2SO_4. Since in the best designed sulphuric acid concentrating units

all of this H_2SO_4 vapor but a small amount is recondensed under such conditions that the heat liberated in condensing is usefully applied, only the heat of vaporization of water will be taken into account, except as noted later.

The heat of dehydration is simply the heat of dilution reversed—that is, there must be put into the solution the same amount of heat, in order to break up hydrates, in concentrating from *a* per cent to *b* per cent, that would be given up by the dilution of the same quantity of H_2SO_4 from *b* per cent to *a* per cent.

The heat of maintained boiling is the summation of the increments of heat necessary to raise the acid to its new, continually higher, boiling points. It is sensible heat, evaluated as the product of a continually decreasing weight, temperature increments between continually increasing boiling points, and a continually decreasing specific heat.

Heat Required Shown Graphically

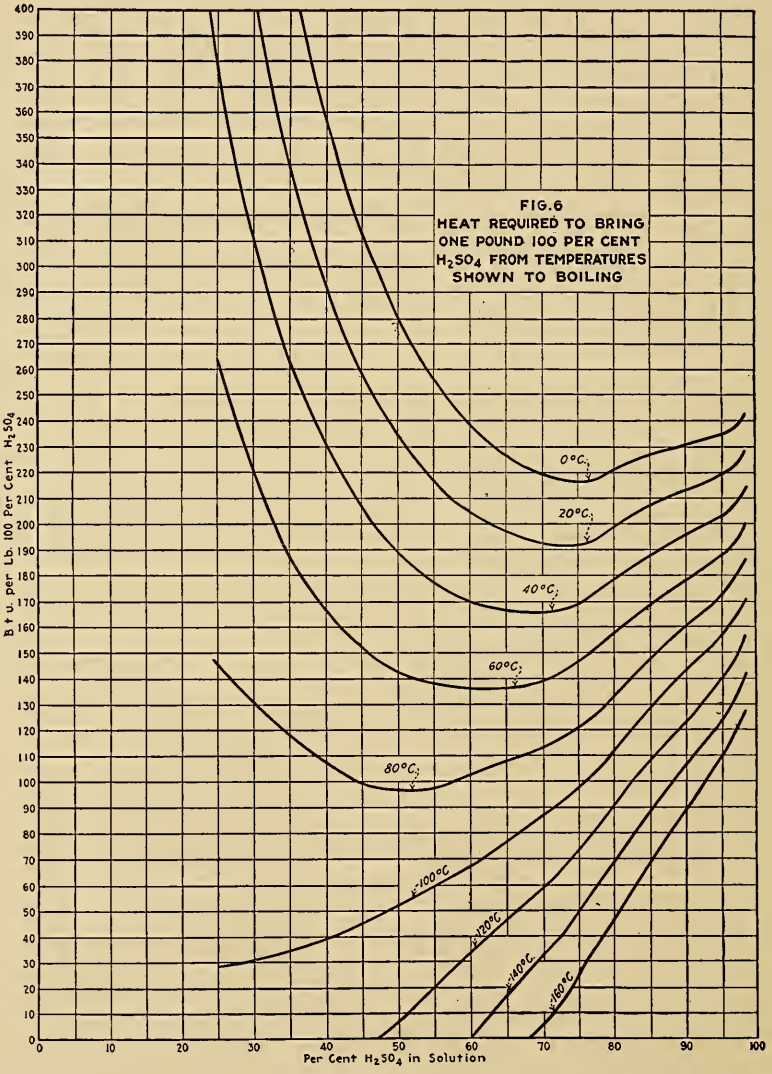
For the convenient use of designers and operators these various values have been calculated over a wide range of concentrations and shown graphically. Fig. 6 shows the sensible heat, H_s, required to bring 1 lb. of 100 lb. H_2SO_4 at any strength from any temperature to the boiling point. It has been calculated using the dotted curve of Fig. 1 and the full curve of Fig. 2.

Fig. 7 shows the heat of vaporization H_v, the heat of dehydration H_d, the heat of maintained boiling H_b, and the total heat H_t, the sum of H_v, H_d and H_b, for 1 lb. of 100 per cent H_2SO_4 concentrated from any strength to 98.5 per cent H_2SO_4. This latter figure has been selected because it is the highest strength of H_2SO_4 solution which can be reached by simple boiling at atmospheric pressure. When this concentration has been reached, both H_2SO_4 and H_2O are driven off from the solution by further boiling in a constant ratio to maintain this strength.

It is, of course, obvious that H_t can be obtained for 1 lb. of H_2SO_4, concentrated from any one strength to any other strength below 98.5 per cent, by simple subtraction.[10] The value of H_t thus obtained added to the value of H_s read directly from Fig. 6 then

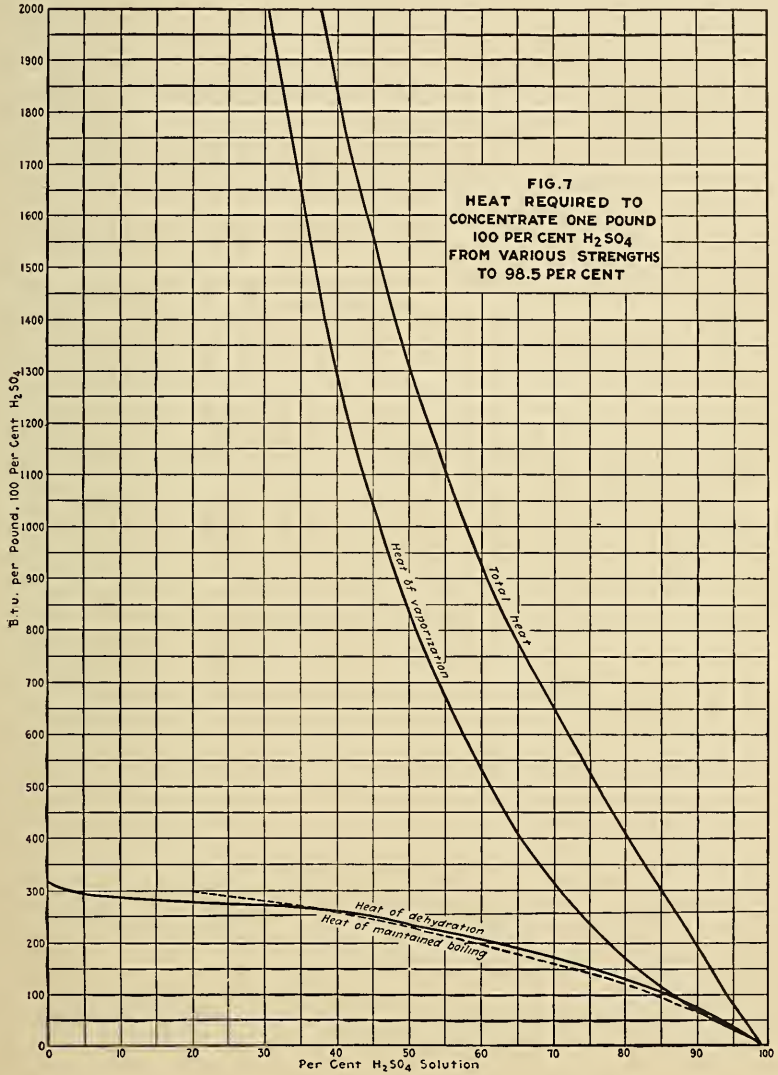
[10] It is noteworthy that the curve Ht is practically a straight line from 65 per cent to 98.5 per cent H_2SO_4 and therefore that less than a 2 per cent error will be introduced by assuming that 23.3 B.t.u. is required per lb. of H_2SO_4 per % difference in this range.

gives the total heat required theoretically to concentrate 1 lb. H_2SO_4 from any concentration and at any original temperature to any other



concentration and boiling temperature at that concentration. This theoretical figure divided by the amount of heat actually used then gives the thermal efficiency of the process, which may be expressed

as a percentage. If the amount of H_2SO_4 lost by evaporation is appreciable, as may be the case with simple concentration in open



pans, then the theoretical figures read from the curves must be increased, as will be shown below.

Illustration of Use of Curves

An example or two will illustrate the method of using the foregoing curves and data. Suppose 60 deg. Bé. sulphuric acid at atmospheric temperature is being concentrated in open pans, with no fume recovery, to 66 deg. Bé., there being required 500 lb. coal, of 13,000 B.t.u. per lb., per ton of finished acid. The recovery is known to amount to 96 per cent. What is the thermal efficiency of the apparatus?

The per cent H_2SO_4 in 60 deg. Bé acid is 77.7; in 66 deg. Bé. acid, 93.2. One ton of finished acid thus contains $2{,}000 \times 0.932 = 1{,}864$ lb. H_2SO_4, which required $500 \times 13{,}000 = 6{,}500{,}000$ B.t.u., or 3,487 B.t.u. per lb. H_2SO_4. One lb. H_2SO_4 in the finished acid corresponds to $1 \div 0.96 = 1.042$ lb. H_2SO_4 in the original acid. To heat 1.042 lb. H_2SO_4 as 77.7 per cent acid from atmospheric temperature, say, 20 deg. C., to boiling, requires, from Fig. 6, 194 B.t.u. $\times 1.042 = 202$ B.t.u. To concentrate 1 lb. H_2SO_4 from 77.7 per cent, and boiling temperature to 93.2 per cent, requires, from Fig. 7, $465 - 122 = 343$ B.t.u. To concentrate 0.042 lb. H_2SO_4 from 77.7 per cent to 98.5 per cent—i.e., completely—requires, from Fig. 7, 465 B.t.u. $\times 0.042 = 20$ B.t.u., exclusive of the heat required to volatilize the H_2SO_4 itself. This would be $0.042 \times 220 = 9$ B.t.u. The total theoretical heat required is hence per lb. finished H_2SO_4:

	B.t.u.
Sensible heat, H_s	202
Total heat, H_t	343
Latent heat of H_2SO_4 lost by evaporation	9
Total heat of this lost H_2SO_4	20
Total theoretical	574
Actually used	3,487

Theoretical thermal efficiency $574 \div 3{,}487 = 16.5$ per cent.

In the case of the surface evaporator described by Mr. Gilchrist of the Chemical Construction Co., 11 gal. of fuel oil will concentrate 1 ton of 66 deg. Bé. acid, starting with 55 deg. Bé. acid at atmospheric temperature.

One ton of 66 deg. Bé. acid contains, as we have seen, 1,864 lb. H_2SO_4. Assuming the fuel oil has a thermal value of 18,000 B.t.u. per lb. and weighs 8 lb. per gal., there is used $18{,}000 \times 8 \times 11 = 1{,}584{,}000$ B.t.u., or 850 B.t.u. per lb. H_2SO_4.

The per cent H_2SO_4 in 55 deg. Bé. acid is 69.7. From Fig. 6,

193 B.t.u. is required to heat 1 lb. H_2SO_4 at this strength from 20 deg. C. to boiling, and from Fig. 7 the concentration from 69.7 to 93.2 per cent requires 663 — 122 = 541 B.t.u. In this case the H_2SO_4 lost is negligible, therefore the total heat theoretically necessary is 193 + 541 = 734 B.t.u. per lb. H_2SO_4. 734 ÷ 850 = 86.3 per cent thermal efficiency.

Numerous other applications of the data contained in the various figures will readily suggest themselves to the reader.

Discussion

President Howard: This paper is now open for discussion.

Mr. Clark: I think Mr. Zeisberg has given a very excellent paper and has shown the practical application of his experiments, so that they may be of very great value.

President Howard: Mr. Gilchrist, have you anything to add?

Mr. Gilchrist: I think it will aid us a very great deal. I examined a copy of the results obtained by Mr. Zeisberg and found that they reached very close to the figures which we obtained.

MODERN METHODS OF CONCENTRATING SULPHURIC ACID

Methods in General Use and a Newly Developed Apparatus of the Submerged Hot Air Type with Particular Reference to Its Application in the Concentration of Separated Sludge Acid from Oil Refining.

By PETER S. GILCHRIST

Read at the Niagara Falls Can. Meeting, June 19, 1922

Considerable study of sulphuric acid concentration has been made by different chemical engineers during the last few years, stimulated, to some extent, by the heavy demand occasioned by the war. Instead of small units of 5 to 10 tons capacity per day, we now think of units of 80 to 125 tons capacity per day, the large units requiring no more labor than was required for the smaller units and, at the same time, operating with greater economy of fuel.

The advent of the Glover tower gave chemical engineers the idea of using the principle of the Glover tower for the higher concentration of acid. To-day the tower system and the combined tower and surface evaporation systems of concentration are the methods in most general use, especially for concentrating chamber acid.

Owners of plants for the concentration of chamber acid, or the reclaiming of contaminated sulphuric acid, are to-day looking for equipment that will operate without too many unnecessary shutdowns for repairs, and that can be operated with the least possible labor.

The principal features to be considered when planning the installation of a concentrator are the following: a reasonable investment for the owner, durability of the equipment, minimum labor, low consumption of fuel and power, high recoveries and elimination of waste fumes.

The use of fuel oil as a heating medium for evaporation, and the perfection of the oil burner so as to get absolute combustion, have made it practicable to apply the direct heating principle for evaporating without discoloring or contaminating the acid.

The use of more permanent construction materials has reduced to

a minimum the maintenance and labor costs. For instance, a vast amount of concentrating is now being done in baths by the direct-heating principle and in towers where the principal item of construction is acid-proof masonry. The adoption of acid-proof iron for overflows and transfer lines for hot strong acids has been very advantageous.

In this paper the antiquated pan, still, and bottle systems are eliminated, confining the description to the following systems: (1) Cascade. (2) Tower system. (3) Combination surface evaporation and tower concentration. (4) Hot air submergence type. These four methods, especially the last three, are the ones used principally in modern plants.

Description of Continuous Cascade System

In this type of concentrator we have the application of indirect heat for evaporation. The heat can be supplied with oil, gas, coal, or coke. The combustion gases do not contaminate the acid, as the pans are heated from the under side, the hot gases not coming in direct contact with the acid. This type consists of a series of pans, or dishes, in several rows, each row a step higher than the preceding one in order that the acid may enter at the top pan and overflow by gravity from one pan or dish to the other until it is sufficiently concentrated. The heat is applied at the acid outlet end, at which place is located the lowest row of pans. The pans or dishes are supported on open seats which are directly exposed to the heat.

The three or four lowest dishes in each series are protected by bowls from the direct heat, so as to prevent violent ebullition and spurting of the acid. The acid vapors are drawn off by an exhauster and condensed. The loss by fumes is likely to be greater with this system than with the tower system. The cascade apparatus is designed so as to get at each dish or pan readily in case of breakage. A cracked or broken pan necessitates an interruption in the flow of acid, in addition to the loss of acid sustained. The advent of the vitreosil dish, which has a very low coefficient of expansion, has very materially reduced the losses by breakage. It is claimed that the breakage of vitreosil dishes is about 5 per cent and the pans 1 per cent. A. E. Wells and D. E. Fogg[1] describe a 10-ton plant with

[1] "The Manufacture of Sulphuric Acid in the United States," Bulletin 184, Department of the Interior, p. 137.

one hundred dishes 12 in. in diameter and 60 preheating pans 24 x 12 in. for concentrating acid from 60 to 66 deg. Bé. They give the cost of concentration as follows:

Coal, 17 per cent at $5.00 per ton	$0.85
Labor	1.25
General expense and repairs	1.00
Loses, 4 per cent of acid, assuming 60 deg. Bé. acid at $8.00 per ton	.30
Operating cost per ton of 66 deg. Bé. from 60 deg. Bé.	$3.40

For comparison with other estimates following in this paper, it is to be noted that 17 per cent of a ton of coal, or 340 lb., is equivalent to 245½ lb. oil, or 32.3 gal. Then 32.3 gal. oil at 4c. per gal. equals $1.29, or an increase of 44c. in fuel cost per ton of acid, making the total cost on the basis of Wells' and Fogg's figures $3.84 per ton.

Description of Combination Cascade and Tower System

Combinations of cascade and tower systems have been used. An installation at Baltimore in 1916, with twelve iron pans 36 in. in diameter, in two rows, produced 23 tons of 66 deg. acid per 24 hours from 54 deg. Bé., the acid entering the top pans being 57 deg. Bé. at 290 deg. F. Actual operating cost per ton of acid is as follows:

Fuel oil, 19.5 gal. at 4c	$0.78
Labor	.71
General expenses and repairs	.85
Losses, 10 per cent of acid, assuming 60 deg. Bé. acid at $8.00 per ton	.80
Operating cost per ton of 66 deg. from 54 deg. Bé.	$3.14

Description of Tower System

In this type of concentrator the entire concentration is done in a tower. The tower is partly filled with suitable tower packing. The combustion gases enter at the bottom of the tower, and as they ascend they meet the downcoming acid in the tower, the exit of steam and gases being made at the top of the tower. The weak acid is sprayed in at the top, and the strong acid settles in a basin at the foot of the tower. It is interesting to note that in this type of concentrator the entire volume of hot air comes in direct contact with the acid, thus keeping the strong acid at its actual boiling point. This has the disadvantage that the hot gases of combustion play directly on the arches and tower packing before the gases have much chance to cool.

The depreciation on the apparatus for this method of concentration is very reasonable, due to the tower being made of acid-proof masonry work, but it is understood that the lower part of the packing has to be renewed occasionally, as it will burn out due to the high heat. Results from this method are claimed to be 1 ton of 66 deg. acid from 60 deg. with 11 to 12 gal. of oil.

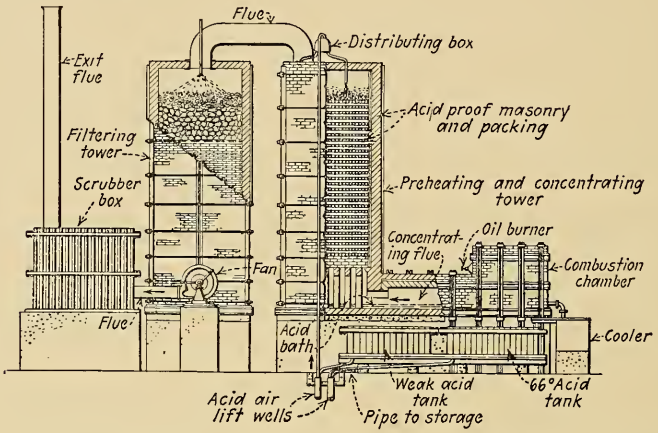


FIG. 1. Combination Surface Evaporation and Tower Type for Concentrating Chamber Acid

DESCRIPTION OF COMBINATION SURFACE EVAPORATION AND TOWER SYSTEM

It was found years ago that the method of surface evaporation, or direct heat application, was much more efficient than the indirect application of heat, such as with pan or still systems. Surface evaporation was not very practical before the advent of the oil burner, as absolute combustion is essential to success. The principle of tower concentration is well known. In this combination type concentration is accomplished (1) by surface evaporation, (2) by tower evaporation and preheating. The weak acid is sprayed in at the top of the tower. The upper portion of the tower does the preheating and the lower portion the preliminary concentration. The tower is packed with suitable packing materials. The acid falls from the tower into a long horizontal flue containing a bath of acid, over which the hot gases pass. The combustion gases enter the flue at the acid outlet end and pass along the surface of the acid to the foot of the tower, where they

pass up through the interstices of the tower packing, meeting the downcoming weak acid. The tower is of sufficient height and size to utilize the remaining sensible heat of the combustion gases. The greater part of the concentration is done in the pan flue, where the acid is brought to maximum strength. The bath of acid is about 9 in. deep, and as the hot gases are brought into immediate contact with the surface acid, the acid takes up the heat much better than when the acid and heat are separated by metal plates, as is the case with cascade or pan systems. Evaporation is very greatly assisted by the direct heat over the acid, as the draft quickly removes the vapors formed. The finished acid leaves the concentrator at the furnace end, temperature about 50 deg. F. below the actual boiling of the acid, which is strong evidence of the efficiency of this system. Because of low heat reaching the tower, the apparatus itself has a very long life and the tower packing proper will last as long as any of the apparatus.

The principal apparatus of this concentrator consists of a combustion chamber, a concentrating pan flue, concentrating tower, filter, and scrubbing tower, all of which are constructed of acid-proof masonry, well braced with steel framing and supported on concrete

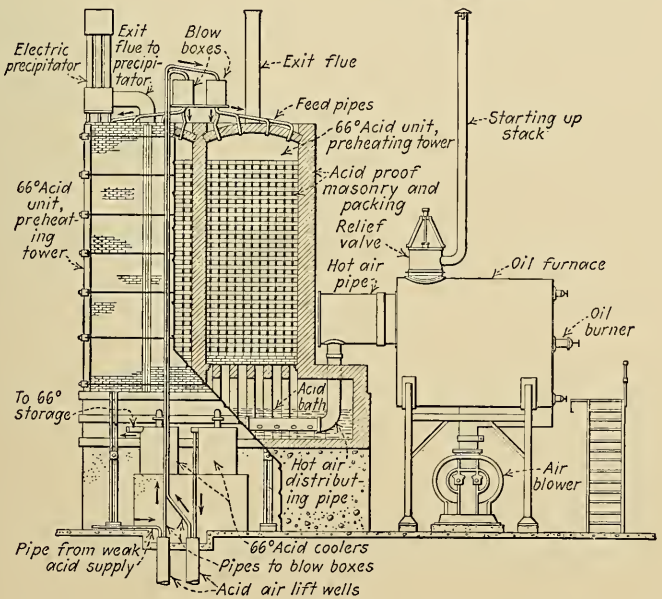


FIG. 2. Hot Air-submergence Type Unit for Concentrating Sludge Acid from Oil Refining

or brick foundations at a suitable height above the ground level. On top of the concrete foundations masonry-lined lead pans are used, on which are built the masonry walls. The concentrating tower is packed with checkered brick, quartz, or other suitable packing, and the filter tower is packed with 3 in. special rings, or quartz. If the packing materials are carefully selected, the distillate from the tower can be sold for battery acid and other similar uses.

Two 50-ton units of this type concentrator were installed nearly 5 years ago at Bayonne, N. J., for the Standard Oil Co. Recent figures have shown that over this protracted period of operation the consumption of oil was from 10 to 11 gal. per ton of 66 deg. acid starting from 55 deg. Bé. During a period of a little more than 4 years over 140,000 tons of 66 deg. acid was turned out with a repair and upkeep cost of less than $10,000. This gives the cost of repairs and upkeep at 7c. to 8c. per ton of 66 deg. acid. One man per shift operates the entire plant. Cost of operation is as follows:

Fuel, 11 gal. at 4c	$0.44
Labor	.12
General expenses and repairs	.30
Losses, 3½ per cent based on $8 per ton of 60 deg. acid	.28
Operating cost per ton of 66 deg. acid from 55 deg. Bé	$1.14

The labor per ton for large plants is naturally less than for small plants.

This system of concentration is especially adaptable for making 98 per cent acid, on account of construction. The apparatus can easily withstand the higher temperatures encountered in the final stage of concentration. In bringing acid to 98 per cent strength provision has to be made for taking care of the additional distillate, and naturally the output of acid decreases and the oil consumption increases.

Description of Hot Air Submergence System

Especially in the concentration of sludge acid it is necessary to accomplish concentration at the lowest possible temperature, because the acid to be concentrated is contaminated with carbonaceous matters which, in company with strong hot acid, quickly causes the breaking up of the acid into SO_2, it being well known that 1 lb. of carbon will break up 16 lb. of acid. Heretofore the pans have been used mostly for the concentration of sludge acid, but the cost is almost prohibitive, and in some cases when using the pan system the cost of concentration

exceeded the cost of new acid. The cost of concentration by this new method of hot air submergence in some instances has reduced the cost of the 66 deg. recovered acid to one-third or one-fourth the cost of new acid.

This hot air submergence type of apparatus is designed to concentrate any kind of sulphuric acid, and especially separated sludge acid of any quality. The underlying principle of the process is concentration by blowing hot air, at a temperature of about 1,200 deg. F., through the acid. The process is continuous except that when handling sludge acid the concentration must be carried out in two stages for reasons stated later.

Operation of Submergence System on Sludge Acid

In concentrating sludge acid from oil refineries the operation is carried out in two stages in order to avoid frothing and foaming due to the decomposition of the hydrocarbons. In the first stage operation the weak acid is fed in at the top of the tower direct from the pumping lines. The pumping and regulation of the acid are done entirely with the well-known acid air lifts. The rate of supply is carefully regulated to control the speed of operation, also the strength and temperature of the acid bath in the concentrator. By controlling the temperature and the quantity of air blown through the acid and the amount of acid fed to the concentrator, the acid in the pan is maintained constantly at from 50 to 55 deg. Bé., or just below the point at which foaming commences. At this strength the acid hydrocarbons are broken down and volatilized by the rapid stream of air passing through the acid. The acid remains constantly at a strength sufficiently low so that carbonaceous matters (tar, oil, etc.) are not attacked, and consequently the losses in the first unit are practically negligible. The acid is drained off continuously, passing through a cooler into intermediate storage tanks, from which it is pumped to the top of the high stage unit for the second stage operation. The operation of the high stage unit is very similar to that of the low stage unit. The acid bath is maintained at 66 deg. Bé. and is drawn off continuously at that strength. The finished acid comes out of the concentrator at about 110 deg. F. below its actual boiling point.

Each unit is provided with a tower packed with checkered brick which serves principally as a preheater.

The hot air is produced by the combustion of oil in a specially

designed combustion furnace which operates under pressure. A blower provides air sufficient for combustion and an excess necessary for the proper regulation of the temperature. The hot air from the combustion chamber passes through a main header to both units and is distributed through manifolds to a point below the acid level in the concentrator bath.

When the air at 1,200 deg. F. is released under the surface of the acid, it quickly gives up its heat and passes out of the bath at a temperature slightly higher than the temperature of the acid. It gives up most of its remaining heat in passing through the preheating tower.

The two units in which the first and second stages of concentration are carried out are of similar construction. The acid bath is con-

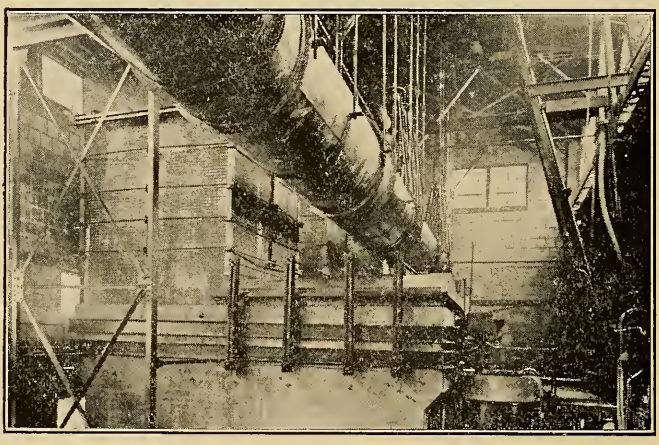


FIG. 3. Separated Sludge Acid Concentrating Plant in Operation

tained in a rectangular lead pan on a raised concrete foundation, the pan being lined with acid-proof brick. About two-thirds of the pan is covered with a chemical brick arch, through which project the acid-proof iron pipes that carry the hot air under the surface of the acid. A tower of acid-proof masonry rises from the rear end of the pan to a height of about 30 ft. This tower is packed with staggered brick and provides sufficient surface for the transfer of the heat from the escaping gases to the incoming acid.

The results over a protracted period of operation have shown the

oil consumption to be around 35 gal. per ton of 66 deg. Bé. acid when starting from acid of 35 deg. Bé. at room temperature. This oil consumption figure includes raising the heat of the acid in the second stage operation. This gives an equivalent of about 9½ to 10 gal. of oil per ton of 66 deg. Bé. acid when starting from 60 deg. Bé. In the lead pan system, besides the expense incurred by frequent repairs to the pans, it has been recorded that it requires 90 to 110 gal. of fuel to concentrate 1 ton of 66 deg. acid when starting from 35 deg. Bé.

One man per shift can operate the largest plant in existence, and the maintenance cost has proved to be around $0.30 per ton of 66 deg. acid.

Comparative cost of concentrating sludge acid by the old and new method is as follows:

Cost of Producing 66 Deg. Acid from 35 Deg. Bé.
Sludge Acid Using Lead Pans and C. I. Stills

100 gal. oil at 4c	$4.00
Labor	.60
General expenses and repairs	2.50
Losses, 20 per cent based on $8 per ton of 60 deg. acid	1.60
Operating cost per ton 66 deg. acid from 35 deg. Bé.	$8.70

Cost of Producing 66 Deg. Acid from 35 Deg. Bé.
Sludge Acid Using Hot Air Submergence Type

35 gal. oil at 4c	$1.40
Labor	.20
General expenses and repairs	1.10
Losses, 6 per cent based on $8 per ton of 60 deg. acid	.48
Royalty	1.00
Operating cost per ton 66 deg. acid from 35 deg. Bé.	$4.18

Sulphuric Acid Gas Recovery

The method of recovering gases has not been touched upon. This is interesting, because the fume trouble has always been an important subject for lawsuits.

In the indirect method of concentration, the escaping gases may be efficiently condensed in water-cooled condensers, but when concentrating by the direct heat method, the escaping gases are of greater volume, for which reason such condensers are impracticable. In general practice a filtering or scrubbing tower is used. These generally consist of towers or large boxes constructed of lead or acid-proof masonry, packed with suitable tower filling, such as coke, hard coal,

quartz, or rings. If the filtering area, or the tower filling, is of large enough volume, and if the filling material itself is efficient, water is not required. In cases where the filtering area is small the gases will be absorbed more efficiently by spraying a little water in at the top of the tower. When using water for filtering, in some cases the strength of the distillate acid varies from 30 to 40 deg. Bé. In efficient towers

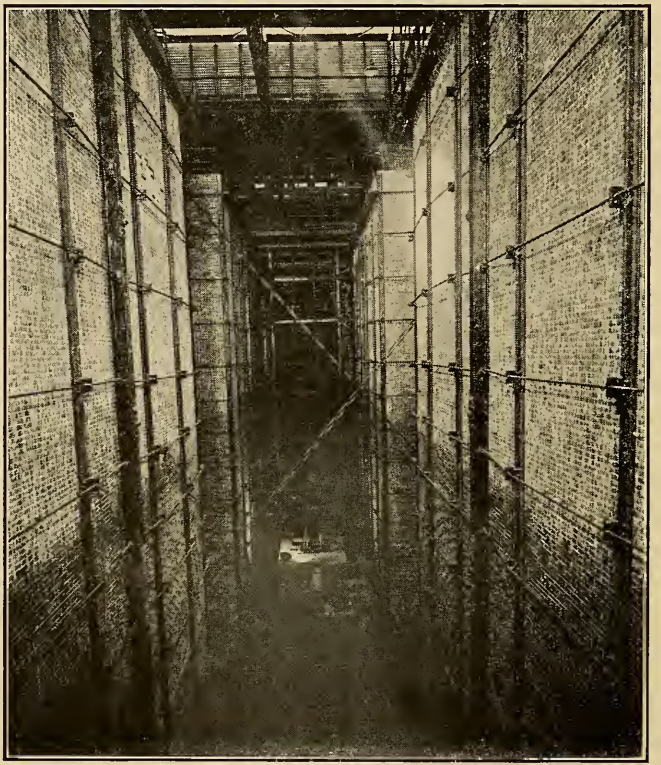


FIG. 4. Nitric Acid Absorption Towers at U. S. Nitrate Plant No. 2

the condensed acid varies in strength from 40 to 55 deg. Bé. when no water is used.

The electric precipitator is being used exclusively for the precipitation of the acid gases in conjunction with hot air submergence type concentrators, whether used for concentrating chamber acid, sludge acid or other contaminated acids. It has also been found very effective on other installations. It looks as if this precipitator will eventu-

ally replace all other gas-filtering methods, as the construction is very simple, the recovery the most perfect, and the cost of operation very little. The acid comes out of the precipitator at from 50 to 60 deg. strength and the recovery in several instances has been recorded at 99 per cent, while the recovery in filtering towers varies from 60 per cent to 95 per cent.

Acid-proof Masonry

The use of acid-proof masonry as a permanent construction material for concentrators has been mentioned several times. The success of this construction for concentrators and for all other kinds of acid absorption and treating towers is assured. The construction requires careful design, the use of superior and proper grades of material, the best workmanship, and the proper curing and treating of the cement, especially in the hot towers for sulphuric acid. The outer walls are constructed of acid-proof shale brick and acid-proof cement, and the inside of tower is lined with several layers of 1-in. chemical tile. Towers thus constructed are very durable and if the work is properly done and the towers properly treated, very little seepage will take place. All masonry towers should be operated under slight vacuum.

Several makes of cement have been used—for example, "Acipruf" as manufactured by the Chemical Construction Co., and "Duro" as used by the Process Engineering Co. In these cements sodium silicate is used as a binder.

The largest example of acid-proof masonry work in this country is the installation of the nitric-acid absorption towers and acid concentrators at government nitrate plants at Sheffield and Muscle Shoals, shown in Fig. 4. In both places combined there were fourteen large towers, each measuring 32 ft. square on the outside and 60 ft. high, each tower being divided into four parts and each part packed in its entirety with "Chemico" spiral packing rings. In these installations it required millions of brick and several thousand tons of "Acipruf" cement. During the operating test period of these towers no leakage whatever developed.

Discussion

President Howard: I should have introduced Mr. Gilchrist to those of you who are not familiar with his line of work, by saying that Mr. Gilchrist is one of the most expert designers and builders of the chamber system for the manufacture of sulphuric acid in this

country. His work has been very largely done in connection with the fertilizer industry, and some of you in different lines, therefore, may not have known him as well as I and thousands of others do know him. This paper is an exceedingly valuable contribution and it is now open for discussion. [No response.] I might say that as far as this submergence type of concentrator is concerned, I was very much interested in it, because a great many years ago, back about 1891, I had some experience along that line, but at that time Durion was not known, and quartz or fused silica was not known, and there were no materials available to make such a process a practical one. I did find out some very interesting facts. I used perforated cast iron pipe submerged under boiling hot 60° B. acid that was being concentrated in lead pans and blew hot air through the pipe, and I found that the hotter the air was that I blew through the acid, the cooler the acid got, which was a very interesting fact, showing that the passage of the hot air, which was much above the normal boiling point of the acid, increased the rate of evaporation of the water in the acid to such an extent that in spite of the fact that heat was being supplied to the lead pans by direct fire underneath, and that the hot air was being blown through the acid at a temperature of several hundred degrees above the boiling acid, the increased rate of evaporation required a so much more rapid conversion of sensible heat into latent heat that the temperature of the hot acid actually dropped very materially. This is a phenomena which Mr. Gilchrist has spoken of a number of times, where the temperature of a highly concentrated acid was a good deal below the boiling point of the acid, showing that evaporation was taking place way below the boiling point, and from the experiments I made at that time it looked as though the hotter the gases were, the cooler the acid would become. The danger in getting the air too hot is that instead of evaporating simply water you evaporate also large quantities of sulphuric acid, but the principle is a very interesting one and I am very much pleased to see it finally worked out. Dr. Reese, can't you say something about this proposition?

Dr. Reese: I have nothing that I can add. I am very much interested in this paper, and one of our men has seen the apparatus in operation. But I do not think I can add anything to what has been said.

President Howard: Mr. Zeisberg, can you say anything?

Mr. Zeisberg: I saw this apparatus operating on sludge acid in Philadelphia and was very much impressed with the smoothness with which it was operating, with the small number of men who could handle the plant, and with the very high recovery which was being obtained on sludge acid, which, as everyone knows who has handled it, is likely to break up on heating. In our own business, we have not gone far with this device, because it is particularly adapted to handling large quantities, and becomes more effective the larger the unit, while the quantities of acid we have to handle are small.

INCREASED CAPACITY OF CASCADE SYSTEMS

By L. A. THIELE

Read at the Niagara Falls Meeting, June 19, 1922

The continuous cascade concentrator originated in the plant of Chance Brothers, Oldbury, England (1871). Before that time sulphuric acid was concentrated in glass retorts holding about 175 lbs. each, which were set in a sand bath on the same level in a galley furnace. Gridley[1] changed this intermittent arrangement into a continuous one by placing these glass retorts terracewise in an obliquely ascending furnace, connecting the retorts by siphons in such a manner that the top retort was fed with fresh acid, which, after being concentrated to some extent, flowed to the next lower retort and so on through the series of 4 or 5, while the concentrated O.V. was continually discharged from the lowest retort, which had its position in the hottest part of the furnace.

While in later years the furnace was greatly enlarged and the large retorts reduced in size and appearance, the principle as originally adapted by Gridley did not change. Porcelain beakers followed the glass retorts and were superseded by fused silica (Vitreosil) dishes in 1906, shallow Vitreosil pans, and dishes and pans of special cast iron, high in silicon, about 1910. More attention also was paid to the preconcentration of the acid before running into the cascade proper, by adding preheaters, long basins, towers, interposing settling tanks and sand filters to cope with muddy acid. The furnace underwent changes owing to different fuels, as coal, coke, gas, and oil. But the most prominent change was in the size and appearance of the cascade dishes or basins, based upon the fact that a more rapid evaporation and consequently larger production was obtained the more the depth of the acid stream was reduced.

Given an increased capacity of the heat generator, it stands to reason that the capacity of a cascade concentrator can only be increased by either increasing the length of the channel or by increasing the heating surface of the cascade dishes or basins.

To increase the heating surface of the cascade basins without

[1] Brit. Pat., 1243, 1871.

lengthening the channel, and at the same time to reduce the depth of acid film running down the cascade, is the purpose of U. S. Patent 1,380,689 (1921), by using basins with corrugated bottom instead of semi-spherical dishes or shallow flat-bottom pans. The size of these basins is 12″ x 12″ x 6″ deep; they have 4 deep corrugations in the botton, as illustrated in the here accompanying drawings, Figs. 1 to 3.

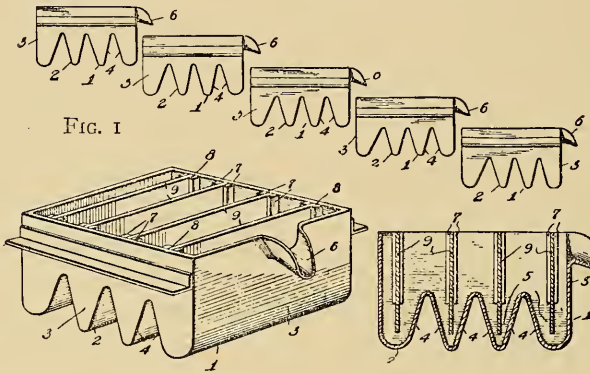


Fig. 1

Fig. 2

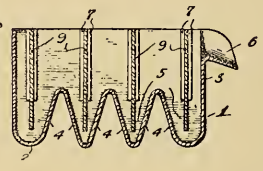


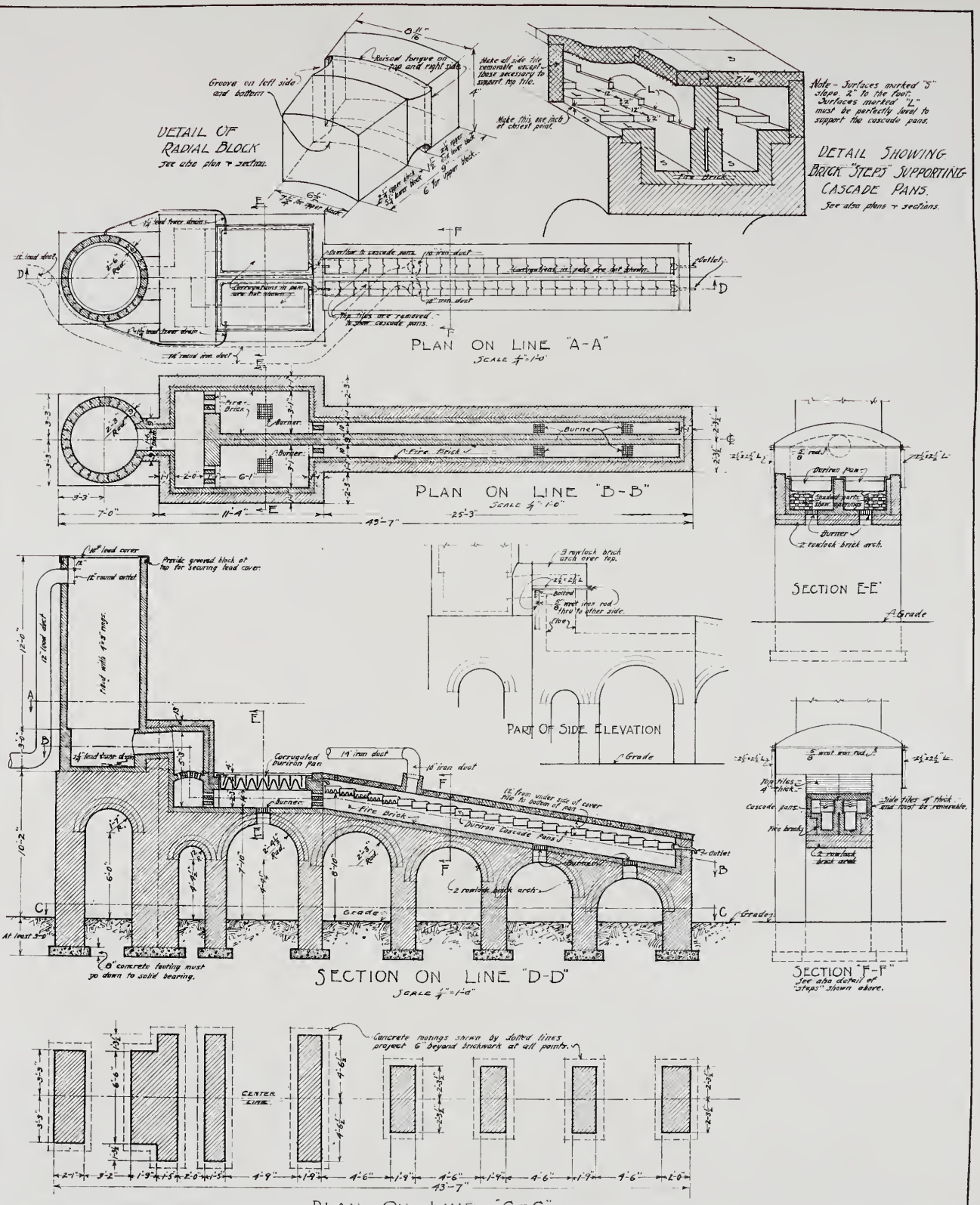
Fig. 3

Within each corrugation a baffle, which is also corrugated at the lower edge dipping into the acid, is interposed, compelling the acid to flow in a wavelike motion through each individual basin in a stream of less than ¾″ in depth on their downward course through the entire length of the channel. As each corrugated basin has an effective heating surface of 3 sq. ft., which is 2½ to 3 times as large as that in dishes or shallow pans respectively, a greatly increased capacity of cascade concentrators is thereby obtained.

A string of 50 of these basins has a capacity of 16 to 18 tons of 92/93 per cent acid, or 12 to 13 tons 95/97 per cent acid per day, with a fuel consumption of 12 to 16 per cent, based upon the weight of the final product.

Fig. 4 illustrates a modern installation.

Continuous cascade concentration is not only applicable to the concentration of sulphuric acid, but to a great variety of other products, such as chloride of zinc and many others, and offers a great advantage in processes of distillation where continuous operation is desirable, as, for instance, in the production of gasoline by the absorption process, or in the extraction of oils, fats, waxes, grease, and the



"TEN" TON SULPHURIC ACID CONCENTRATION PLANT + PATENTS PENDING + U.S. 1,380,689 (June 7.21)

LUDWIG A. THIELE + CHEMICAL ENGINEER

COLUMBUS + OHIO

FIG. 4

like, where the oil has to be freed from the volatile solvent; or for solvent recovery in general.

The following illustrations, numbered Fig. 5 to Fig. 8, illustrate the application of the cascade principle for a "Continuous-Cascade-

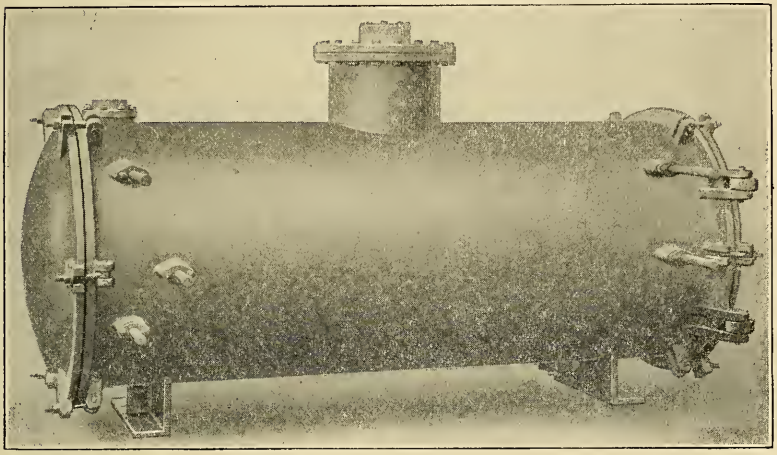


Fig. 5

Steam-Still." Fig. 5 shows the general appearance of the still; Fig. 6 gives an inside view, while Fig. 7 and Fig. 8 show the corrugated cascade basins completely equipped with baffles and heating coil,

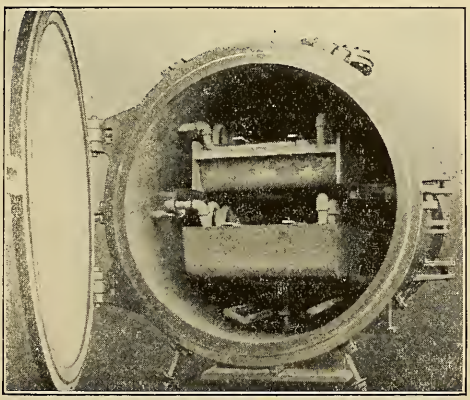


Fig. 6

with and without the baffles in place; Fig. 9 is the coil which fits into each corrugation and sits between each baffle.

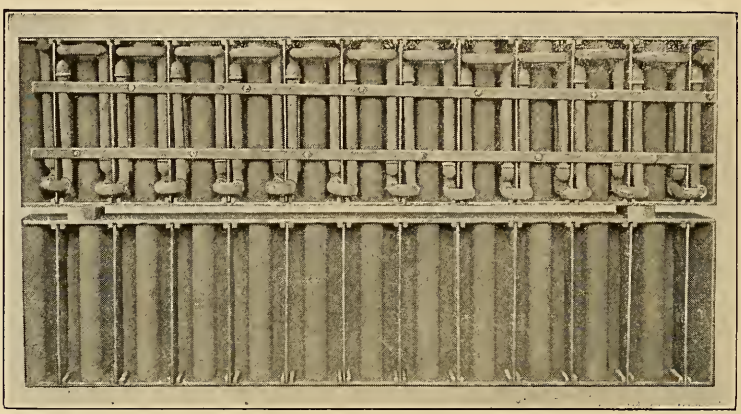


FIG. 7

Two or more of the larger cascade basins, such as are used in preheating acid, are placed horizontally, one over the other into a pros-

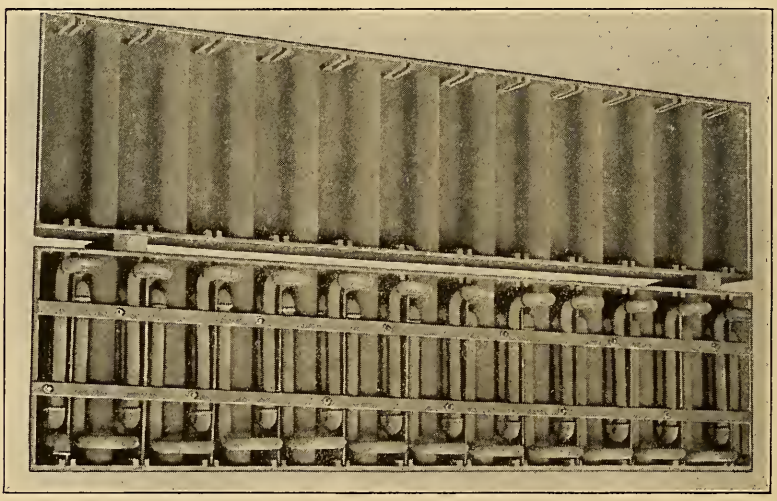


FIG. 8

trate tank. Steam circulates through each coil in each cascade basin; in the bottom of the still a perforated steam coil is arranged and an outlet cage for oil is provided, as well as a tap for water.

The oil, charged, e.g. with gasoline, flows in the first corrugation of the top cascade basin, describes a wavelike motion around and between the steam coils until it reaches the end of the basin, when it overflows to the next lower basin, continuing on its course until it arrives at the bottom, where it comes into contact with live steam, whereby the last traces of volatile solvent are liberated. The oil flows off through the cage and re-enters the circuit, while the gasoline vapors leave at the top of the still to be condensed in a separate condenser.

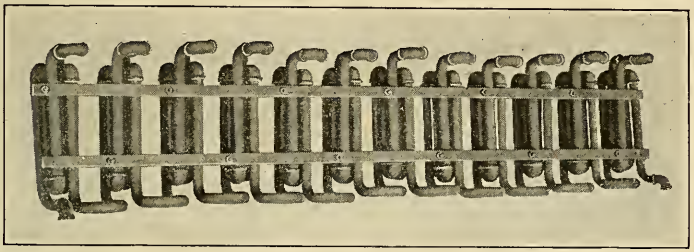


FIG. 9

The still shown in these illustrations has a diameter of 3′–6″ x 9′ long, contains 150 sq. ft. of effective heating surface, and a capacity of 2,500 gallons per hour when using steam of 90 lbs. pressure. Gasoline vapors are liberated in fifteen minutes from the time the oil enters the still.

DISCUSSION

PRESIDENT HOWARD: This paper is open for discussion.

DR. MARSHALL: I would like to make a few corrections of Dr. Thiele's paper in regard to dates. Dr. Thiele says the first silica plant was installed in 1906. As a matter of fact the first complete installation was in December, 1907, in London. That was the first fused silica cascade plant ever built. The beaker type cascade concentration plant using porcelain preceded the dish cascade and dates back to about 1895. The corrugated bottom dish that Dr. Thiele speaks of was used at the works of Rand J. Garroway in Glasgow in 1911. The quartz dishes were about 12 by 24 by 6, with six corrugations in the bottom.

SHRINKAGE OF QUARTZ PACKING IN THE GLOVER TOWER

By Lyle J. Michael and James R. Withrow

Read at the Niagara Falls Meeting, June 19, 1922.

Summary of Scope and Findings

This report deals with suggestions advanced to explain the disappearance of a portion of the quartz packing in a Glover or hot tower. We were disposed to scout the solubility idea which had been advanced. Our results, however, indicate:

1. Quartz is slightly soluble or wastes away in nitroso-sulphuric acid, and in ordinary sulphuric acid, free from oxides of nitrogen. At 150° C. it appears also soluble in C. P. sulphuric acid.

2. Our comparisons of solubility of quartz rock at different temperatures gave no very pronounced temperature effect.

3. The solubility, or at least the rate of solution, increases with what probably is fineness of the particles, though it may be due to actual difference in the silica itself: thus, filtercel has a solubility about ten times that of tower packing quartz ground to one-hundred-mesh. It seems evident that the large pieces of quartz used in tower packing would have a much lower rate of solution than found with the one-hundred-mesh test sample.

4. An analysis of sediment from Glover Tower acid indicates that it is largely lead, with much silica present as fine particles, perhaps abraded or chipped from the packing and washed down by the acid.

5. It is not safe to conclude that the solubility of quartz in acid is entirely insufficient to account for any perceptible shrinkage. Nevertheless it is probable that solubility, or wastage, by acid circulation is a minor factor only in packing shrinkage.

6. It is concluded that creeping and settling effects during changes from alternate hot and cool periods during the life of the tower are the most likely causes of tower packing shrinkage.

Introduction—Quartz Shrinkage

Every once in a while there grows up among the observant operatives of chemical and other manufacturing plants a series of traditions,

observations, narrated ideas of behavior or efficiency of plant or equipment, or even outright superstitions, about the plant. The prudent engineer is not disturbed by these psychological phenomena; he may good-naturedly smile at them, but he always tries to fathom their origin. By this means he frequently finds out little. Sometimes, however, he gets information which his time of association with the matter did not give opportunity to observe. These workmen are often keen observers. Sometimes the engineer gets real ideas as a result of attention to these ever-watchful every-day observers in his plant.

This quartz solubility explanation was one of these ideas or hallucinations laid before us by the acid maker in such insistent fashion as to demand proof that the idea was wrong. A new plant tower had within two years experienced a shrinkage in height of almost two feet in its quartz tower packing. The tower had been packed with standard white, North Carolina quartz, of the grade usually used in this work. Upon being reopened for repairs the tower was found decidedly short of quartz and more had to be added. It was then recalled that there had been a gray sediment in the acid which might have been silicic acid.

Our personal skepticism was not an acceptable answer. Resort was, therefore, made to experimental investigation.

Quartz tower packing has long been in use particularly in the hot, or Glover, tower. Few materials, if any, have an equal reputation for stability under these exacting conditions. Few substances appear to contaminate the acid as little as this packing. We have found no one calling attention to quartz packing solubility or wastage from any cause, and in numerous towers which we have seen opened we never saw evidence of quartz disappearance.

For many years analytical chemists have recognized that silica is soluble in water, HCl and H_2SO_4, to an extent that for even rather crude analytical work can not be neglected.[1] However, this applies to silica as a gel or in finely divided flakes. The mineral quartz could hardly be expected to behave in this way. No data on this were available to us and perhaps no one has investigated the question with tower conditions in mind.

[1] Hillebrand, *J. Am. Chem. Soc.*, 24, 362 (1902); Wunder and Suleimann, *J. Soc. Chem. Ind.*, 33, 279 (1914); Lenher and Merril, *J. Am. Chem. Soc.*, 39, 2630 (1917).

Experimental Tests on Wastage of Quartz

Quartz.—The quartz tested was taken from the supply used by the sulphuric acid plant to pack its towers. This was stated to be North Carolina quartz, which showed a SiO_2 content of 99.6 per cent upon volatilization with hydrofluoric and sulphuric acids. The rock was ground to 100-mesh, washed with dilute HCl and then with water, and dried in an oven. This sample was kept in a glass-stoppered bottle and from it all the samples of quartz used in the digestions were taken.

Acids.—The acids tested as solvents were:

(1) Nitroso-sulphuric acid, obtained from the tank supplying the Glover tower of the acid plant. This acid analyzed:

Sp. gr.	1.670 at 20° C.
H_2SO_4	73.25
HNO_3 and N_2O_3	2.61%
N_2O_3	0.36%

(2) Sulphuric acid, no oxides of nitrogen, Sp. gr. 1.720.

(3) Sulphuric acid C. P., Sp. gr. 1.84.

Method of Determining the Wastage.—Approximately 1 g. samples of quartz were weighed and placed in 300 c.c. Kjeldahl flasks to which short condensers were attached by plaster of Paris, which also served to support the thermometers. The plaster of Paris was mixed with a vinegar solution to retard its setting. When the flask and condenser were set up, 100 c.c. of the acid were introduced into the apparatus and the heating begun. The source of heat was a Bunsen flame regulated to give a fairly even temperature. Since the local conditions were such that continuous long-time runs could not be made, the heating was maintained for from two to nine hours, the apparatus allowed to cool, and then heated up again for another period. The total number of hours any sample was digested at a given temperature does not represent the total time the rock was in contact with the acid. When the run had been heated an arbitrary length of time, the condenser and thermometer were removed and the rock washed into a previously prepared Gooch crucible, fitted with an asbestos mat which had been washed with H_2SO_4, and dried. The crucible was then dried and ignited to constant weight and the loss in the weight of the sample of rock taken as the amount dissolved or

carried through the filter in a state of fine suspension by the acid digestion. These results give a more exact measure of possible quartz wastage than could be derived from solubility determinations made by customary laboratory methods. The latter might be misleading.

The various series of experiments tried follow:

Series I.—Quartz in nitroso-sulphuric acid (Sp. gr. 1.670).

Temperature	Hours Heated	Length of Periods	Wastage per Liter
50° C.....	25	4–9 hours	0.02 gm. 0.003 gm. 0.021 gm.
150° C.....	15	2–5 hours	0.019 gm. 0.014 gm.
	100	2–9 hours	0.146 gm. 0.021 gm.

Series II.—Quartz in sulphuric acid (Sp. gr. 1.670). Heated to boiling point of acid (210° C.). At the end of each two-hour period the loss in weight of the quartz was determined, and then a fresh sample of quartz added to the acid and the digestion continued two hours longer, etc.

Sample Number	First Two-hour Period	Second Two-hour Period	Third Two-hour Period	Temp.
1.....	0.155 g. per l.	0.073 g. per l.	0.120 g. per l.	210
2.....	0.126 g. per l.	0.096 g. per l.	0.102 g. per l.	"
3.....	0.098 g. per l.	0.062 g. per l.	0.065 g. per l.	"

Series III.—Quartz in C. P. H_2SO_4 (Sp. gr. 1.84).

Temp.	Hours Heated	Length of Periods	Solubility per Liter
1. 50° C.....	31	2–9	Slight gain in wt.
2. 50° C.....	31	2–9	Slight gain in wt.
3. 150° C.....	43	3–9	0.138
4. 150° C.....	43	3–9	0.166

Series IV.—Filter-cel (99.96 per cent SiO_2—very fine) in nitroso-sulphuric acid (Sp. gr. 1.670).

Temp.	Hours Heated	Length of Periods	Solubility per Liter
1. 150° C.....	37	2–9	1.096
2. 150° C.....	37	2–9	1.129

Discussion of Results.—Since one-gram samples and 100 c.c. of acid were used, the solubility per liter becomes per cent dissolved by moving the decimal one figure to the right. Obviously there are analytical variations among some of the results which might possibly be eliminated by a more refined technique, though the method adopted of direct loss determination is much more accurate in itself than the usual refined solubility methods. These results show a widely varying loss. They begin at no loss at all at 50° C. after thirty-one hours, or as low in the next lowest case as 0.03 per cent loss in weight in twenty-five hours at 50° C., to as high as 1.66 per cent loss at 150° C. in forty-three hours. Whether this loss in weight of the silica rock was a true solubility effect, or an abrading effect which wasted away the rock as a fine suspension in the acid, was not investigated. Whatever the true nature of the effect, its magnitude was at times sufficient to account for a very considerable portion, if not all, of the shrinkage in question. However, our solubility or wastage effect on 100-mesh rock was a much more severe effect than could ever take place in the large pieces in a tower, and many of our results even on fine material are of insufficient magnitude to account of any substantial part of the shrinkage.

Acid Sediment Investigation

A sediment was observed to settle out of the acid that had been used to digest the quartz, so we investigated the sediment that settles out of the acid coming from the Glover tower. For this purpose a sample of this sediment was obtained from the sulphuric acid plant and analyzed. Under the microscope this sediment seemed to be made up of small metallic bodies, small pieces of sand, and a gray powder. The lead present was determined and reported as sulphate, since the free lead could not be well separated from the combined. The oxides of iron and aluminum are reported together and the SiO_2 was determined by volatilizing the insoluble residue with hydrofluoric acid. This sediment was not necessarily only those particles which settled out of solution in the acid, but a part of it may have been washed from the tower packing by a process of "weathering" as well as by solution. Analysis of this sediment follows:

	Per cent
Lead, as sulfate	61.0
Iron and aluminum oxides	8.3
SiO_2	20.36

It seems, therefore, a fair conclusion that, under the highly favorable condition of extreme fineness, we may reach a wastage of quartz rock which would account for the shrinkage in packing observed.

Rate of solution is usually lost sight of in discussing chemical phenomena. Solubility seems of the greater moment. This is frequently a mistake. Rate of solution is frequently a vital matter in industrial operations. This is probably one of these cases where rate of solution is the vital matter.

Shrinkage as a Chemical vs. a Mechanical Effect

Rate of solution could probably be agreed to be largely a surface phenomenon, other factors being equal. That is to say, of two trials on the same sample of quartz rock, that one would go much more rapidly into solution which was ground finer, because of the greatly increased surface exposed to the dissolving or abrading liquid. If this postulate is correct, then it would also be correct to conclude that the enormously larger pieces of quartz rock used in tower packing, as compared with the one-hundred-mesh rock used to produce the more severe conditions, would undoubtedly show a very slow rate of solution; so slow, in fact, as reasonably to remove this factor from blame for the shrinkage in tower packing observed. Trial of these ideas on large pieces of quartz actually showed that the rate of quartz wastage was greatly reduced the larger the pieces of quartz.

If these ideas hold true, some other explanation must account for the shrinkage. This conclusion regarding wastage or solubility as a cause drives us to the one which presented itself when the matter was first studied, namely: that the shrinkage was probably caused by mechanical or operating conditions solely. The history of this particular plant was such as to occasion numerous shut-downs. These shut-downs naturally involved the cooling of the towers. Cooling would obviously result in the contraction of the packing. This contraction would proceed in a vertical direction as well as laterally, and probably the greater portion of the contraction, because of the load, would be in a vertical direction. Upon again throwing the tower into service, with its subsequent heating up, expansion would take place in all directions, but preferably, laterally, because of the load in the

vertical direction. The repetition of this cycle would result in three things:

1. There would be an apparent shrinkage in the volume and an actual shrinkage in the height of the tower packing.

2. There would arise a much more tightly packed condition within the tower, which would tend to diminish the height of the tower packing.

3. There might arise pressure laterally against the walls of the tower.

The tower packing actually did shrink in height, and the third contingent was the precise thing which caused the examination of the tower and which disclosed the apparent shrinkage; in other words, the tower had begun to swell as a consequence of lateral pressure within the tower packing, and this pressure was so great as to damage the brick walls of the tower and cause leakage demanding repair.

It is quite evident, therefore, that if we had the weight of the quartz originally within the tower, we would probably find it scarcely at all diminished, although the volume had been apparently diminished.

Conclusion

In conclusion, we believe, therefore, that we were probably wrong in our early assumption that the solubility or rate of solution or wastage factor of quartz rock would be entirely too low to account for any shrinkage. Though we never before saw or heard of evidence of serious solubility or wastage of quartz tower packing from any cause, nevertheless our results show that under some conditions this rate of solution or wastage factor is ample to account for the shrinkage. From our work this would not be true under operating conditions. Alternate heating and cooling are more probably the cause of the apparent shrinkage in this case, and also destroyed the tower.

Laboratory Industrial Chemistry,
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Discussion

President Howard: This paper is now open for discussion. Mr. O'Brien, have you had any experience in that line?

Mr. O'Brien: I think I fully agree with the suggestion that it is mostly a matter of heating bringing about contraction and expansion. The only thing I might add is that I might ascribe some effect to

fluorine, but outside of that it is mostly a question of heat expansion and contraction, and not a question of chemical action.

MR. ZEISBERG: In regard to Mr. O'Brien's statement that the presence of hydrofluoric acid might account for some of the shrinkage, I might say that we have operated denitrating towers without any indication of the expansion and contraction effects mentioned in the paper. However, the thermometers at the top of these denitrating towers have often been etched so rapidly by hydrofluoric acid in the gas that sometimes at the end of a few days the mercury was lost out of them. Unless the actual gases are examined I do not think you can say definitely that the quartz is insoluble, as it may be attacked by hydrofluoric acid to produce volatile silicon tetrafluoride.

PRESIDENT HOWARD: Is there any further discussion?

MR. GRAHAM: I quite agree with the remarks by Mr. Zeisberg. In a good many ores that I have come in contact with there is evidence of fluorine, and I think it has a considerable effect on shrinkage.

DR. REESE: There is no doubt of the presence of fluorine in ores. I have had experience in many forms and am fully confident of it.

MR. LEVERETT: I had occasion at one time to check up on the subject of corrosion in an industrial plant. The brick in the kiln showed indisputable evidence of deterioration by fluorine. As successive samples were taken it showed nearer the center of the brick and the same is true of the tower.

PRESIDENT HOWARD: Any further discussion? This point which was brought up regarding the presence of fluorine I think is a very interesting one. I don't think that pyrite ores in this country contain as much fluoride as some of the foreign ones, but it may be of interest simply to comment at this time that in the Russian contact process, the Tenteleff sulphuric acid process, this was developed on Swedish and Norwegian ores, which were quite rich in fluorides, and they were confronted with the necessity of removing considerable quantities of hydrofluoric acid in their purification process. For this they developed a scrubbing process in which they scrubbed the gases in sodium bisulphite which absolutely fixed the fluorine as sodium fluoride, the sulphuric acid having been taken out previously by another scrubbing arrangement. So that if you come in contact with ores with fluorine and want to get rid of the fluorine, you will find a good deal of information in the Tenteleff patents taken out under the name of Eschellmann and Harmuth.

JAMES R. WITHROW:[1] I am glad to find that Mr. O'Brien's experience agrees with our suggestions. The probability that the heating and cooling, because of a series of shut-downs, accounts for contraction and expansion, which would give the appearance of tower packing shrinkage, is thus given weight. It is probable, as the paper shows, that the shrinkage was an apparent shrinkage only.

Regarding the Probability of Action by Fluorine

This is an important matter in the minds of some operators, but probably did not exist in our case for the reason that the source of the gas was mainly elemental sulphur, although some Spanish pyrites was used in the early life of the tower. In this connection, however, it should be stated that two companion plants operated on identical raw materials, and in one case from the same stock pile of ore, and no such tower shrinkage was noticed. These plants did not have shut-down conditions. This again, in our opinion, bears out the conclusions at which we arrived. We found no evidence of hydrofluoric acid. Even our check weights on digestion flasks show no loss upon the long digestions.

It would have been unfair to anyone disposed to doubt our mechanical theory for us to have suppressed the fact that we found evidence of the ability of sulphuric acid and its contaminants to shrink or waste quartz either by solubility or corrosion under certain conditions. The solubility wastage factor was apparently enough at times in our work to account for the shrinkage in this case, although this is not completely proven. The criticism is, therefore, to some extent justified that our results tend to show a solubility basis for the shrinkage, rather than our mechanical theory.

It is interesting to note that the discussion did not bring out a case where such shrinkage as we experienced came from hydrofluoric acid.

It is too bad that there is not a better discussion of the whole fluorine situation in the technical literature. The presence of minute traces of this gas in acid has doubtless caused many difficulties because its presence or effects have been unsuspected. It may have been a factor in our case, but the evidence given above points that it was not a factor at all. I might state that we made measurements which were not included in our paper for brevity's sake. At one time we investigated the amount of the glass flasks which was dissolved, and

[1] Discussion communicated.

we in no case found such solubility. Hydrofluoric acid was, therefore, not present at that time.

Mr. Zeisberg states that they have operated denitrating towers without indication of expansion or contraction effects, but doubtless these were not on the same scale as the Glover tower of the sulphuric acid plant. However, even if they were on such a scale, it is also true that we have operated many Glover towers without this expansion and contraction effect, so that this is not an argument in either direction, as it is not normally the custom to operate Glover towers intermittently as happened in our case. It is only upon the occasion of a series of accidents or breakdowns that opportunity for such expansion and contraction occurs in a hot tower.

The incident of the rapid deterioration of the glass of thermometers in the tops of denitrating towers mentioned by Mr. Zeisberg is probably strong evidence of traces of hydrofluoric acid. I have also had the experience, however, that mixtures of sulphuric and nitric acids have a similar action in the absence of hydrofluoric acid. In fact, this used to be a method of testing chemical glassware to ascertain whether our formula in manufacture was giving us the maximum resistance to chemical corrosion. It is astonishing to find the ease with which such a mixture etches glass made from certain glass formulas, with but slight variation from the suitable formula.

In a subsequent communication Mr. Zeisberg calls attention to the fact that the "solubility" effect found may really have been volatility. This would certainly be true if hydrofluoric acid were the cause. At least it would not be true solubility of quartz in the chemicals, but a kind of chemical solubility or destruction of the original quartz, probably resulting ultimately in at least a partial volatilization as silicon tetra-fluoride. Our idea of "wastage" should probably have been more emphasized.

Mr. Zeisberg has also communicated the idea that the true solubility of quartz in the reagents should have been determined by analysis of the resulting acid. This would have been more difficult than at first appears, as the paper itself indicates. Then, too, the results from apparently precise procedure would have really been inaccurate and therefore misleading. In our opinion, with a material like quartz, our direct determination of loss in weight was the most precise procedure possible. It was adopted to avoid data which would mislead. We were not interested in solubility as a technical

fact. We were interested in loss of quartz or wastage. The word wastage was not entirely satisfactory, and we have also called this loss "solubility-wastage" and also solubility. This latter is technically not correct, as Mr. Zeisberg points out. We also discovered early in the work that the quartz splintered and lost weight by semi-dispersion, and therefore true solubility could not be determined if we had desired it.

We found it not easy to tell definitely what happened to the quartz even when it disappeared. To this we have called attention in our paper. We have been careful to indicate that we prefer the word "wastage" to avoid getting it mixed up with the idea of solubility. There is a clear difference between these two ideas, and we are fairly convinced that this is not a true solubility effect, and, therefore, carefully avoided the usual procedure for solubility determination and made direct measurements of wastage. We did not investigate the possible causes of such wastage, but merely pointed out that it could exist. If we had used the ordinary methods of solubility determination, we would have probably been in error in our conclusions. We also certainly would have misled others, for the fact is becoming better recognized than it used to be that the determination of the existence of a substance in a liquid is not complete evidence of true solubility, and for this reason many of our solubility determinations as they exist in the literature are in error, and must be some day revised. The whole series of collodial dispersoids are a case in point.

THE PRODUCTION OF NITROGEN AND HYDROGEN FOR SYNTHETIC AMMONIA MANUFACTURE

By HUGH S. TAYLOR

Professor of Physical Chemistry, Princeton University

Read at the Buffalo Meeting, June, 1922.

The production of 1 ton (2,000 lb.) of fixed nitrogen, as ammonia, involves the theoretical consumption of approximately 430 lb., or more than 82,000 cu. ft., of hydrogen, measured at ordinary temperatures and pressures. One-third of this volume of nitrogen is also required, which may be in part produced simultaneously with the hydrogen or may be wholly supplied from a nitrogen producing plant. The German synthetic ammonia plants in 1918 had a capacity of 650 metric tons per day. The process is now operated on a technical scale in the United States (at Syracuse, N. Y.) and is being developed in France, England, and Norway. The importance of this division of gas technology is, therefore, readily grasped.

The gas mixture is required for the synthetic operation in a high state of purity. Inert gases, such as the argon group and methane, act as diluents and, in a circulatory system, necessitate a periodical blowing-off and loss of gas in order that the inert constituents do not accumulate beyond a working maximum. Water vapor, oxygen, carbon dioxide, and carbon monoxide are catalyst poisons which, when present continuously in concentrations of 0.01 to 0.1 per cent, lower the efficiency of the synthesis quite markedly. Hydrogen sulphide and sulphur compounds are permanent catalyst poisons, cumulative in effect and eventually necessitating, if permitted to intrude, a renewal of the ammonia-making catalyst.

As a result of the large volume requirements of gas and the high purity essential to successful synthesis, the problem of preparation of the gas mixture is the most important in the cycle of operations from elementary nitrogen to fixed nitrogen product, whether this be ammonia, nitric acid, oxides of nitrogen, ammonium sulphate, or other fertilizer compound. It has been computed[1] that the preparation of

[1] Nitrogen Products Committee Report, British Munitions Inventions Department.

the compressed nitrogen-hydrogen mixture involves as much as 75 per cent of the total cost of the ammonia produced. The attention which has been paid in past discussions to the actual synthetic operation as compared to the gas preparation is out of all proportion to its relative importance and cost in the cycle of reactions. Recent literature abounds in discussion and reports of the ammonia-making processes. Scant attention has been paid to hydrogen and nitrogen technology.

A Review of Existing and Possible Processes

The Liquefaction Process

The earliest synthetic ammonia plant, the Badische Co., at Oppau, operated on hydrogen obtained from water gas at 20 atmospheres pressure by liquefaction of the carbon monoxide, in a liquefaction system of the Linde type, diagrammatically shown in Fig. 1. The

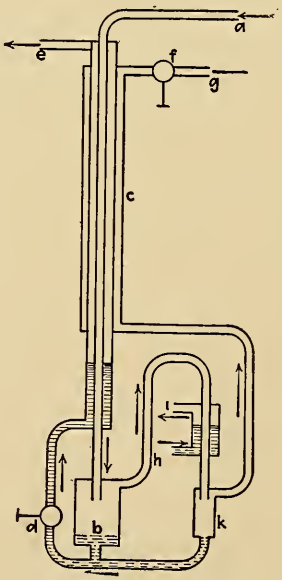


Fig. 1. Linde Liquefaction System for Hydrogen Purification

nitrogen was obtained by fractionation of the liquid air, *h*, *i*, boiling under a partial vacuum, used to establish the low temperature (—205

deg. C.) necessary for the separation of the carbon monoxide from the hydrogen. The carbon monoxide was employed, after being vaporized, to drive a gas engine and thus produce the power requisite for compression of the water gas and of the air employed in the liquid air cooling system. Also, the power requirements for a pressure water scrubber to remove carbon dioxide and an ammonia refrigeration system to remove water vapor were supplied from the same source.

The normal purity of the hydrogen obtained corresponds closely to a gas of the following composition: $H_2 = 97$ to 97.5; $CO = 2$ to 1.7; $N_2 = 1$ to 0.85 per cent. Approximately 40 per cent by volume of the original water gas is received in this form from the liquefaction system. This gas, before use in ammonia synthesis, must be freed from the residual carbon monoxide, this being achieved of late by the Badische Co. by solution in ammoniacal cuprous formate under a pressure of 200 atmospheres. In the earlier stages of the process the carbon monoxide was absorbed at 200 atmospheres in hot caustic soda solution with the formation of alkali formates. Thus purified, the hydrogen residue contains less than 0.1 per cent carbon monoxide and admixed with the theoretical ratio of nitrogen from the liquefaction system was so used in the synthetic operation.

The Water Gas Catalytic Process

The liquefaction process was discarded at Oppau in favor of the water gas catalytic process. In essentials this process consists of the oxidation at 500 deg. C. of the carbon monoxide in water gas by steam in the presence of a catalyst (oxide of iron), the reaction occurring being representable by the equation

$$H_2 + CO + H_2O = 2H_2 + CO_2,$$
Water gas.

The reaction is an equilibrium process and the final composition of the gas is dependent on the steam-water gas ratio, the temperature of operation, and the efficiency of the catalyst. Furthermore, by using water gas admixed with semi-water gas (a gas containing the products of both air-blow and steam-run in the water gas process) a product may be obtained containing the bulk of the nitrogen required in the subsequent synthesis, requiring only small amounts of nitrogen from the liquefaction of air for purposes of exact ratio adjustment.

Details of plant, materials, engineering, and operation of this process have already been discussed before this society,[2] so it is not necessary to recapitulate such in this article. Fig. 2 shows the process diagrammatically. Emphasis need only be laid on the factor which accounted for the change from the liquefaction process to the catalytic process. The factor involved is the water gas: hydrogen ratio or, in other words, the ratio of fuel consumption to hydrogen yield in the two processes. Whereas somewhat less than 40 per cent by volume of the original water gas is received as hydrogen in the liquefaction

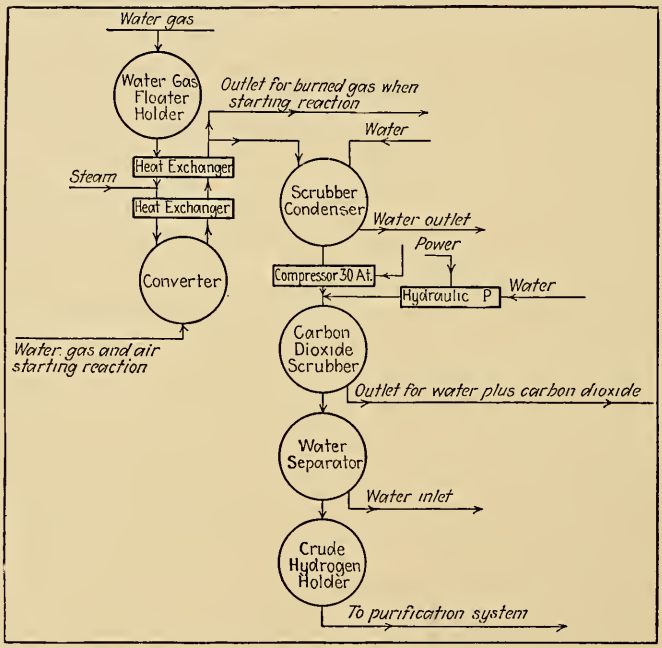


FIG. 2. Flow Sheet of the Water Gas-Catalytic Process

process, the yield in the catalytic process, as can readily be seen from the previous equation, is equal theoretically to that of the water gas consumed. In actual practice it is possible to receive unit volume of hydrogen by the expenditure of 1.25 volumes of water gas. The fuel bill, therefore, should be just one-half that obtaining in the liquefaction process. The purity of the product corresponds approximately

[2] Tour, *Chem. & Met.*, vol. 26, p. 245, *Trans. Am. Inst. Chem. Eng.*, vol. 13, Part II, p. 273.

to that from the liquefaction process, so that no advantages accrue to the catalytic process in that respect.

The Steam-Iron Process

The industry of oil hydrogenation for the production of soap stock and of edible fats has made but little use of hydrogen from either of these two sources. This should, in the main, be attributed to the nitrogen and carbon monoxide present in the hydrogen so obtained. In ammonia synthesis nitrogen is a reactant; in oil hardening it is a troublesome inert, present to the extent of several per cent, depending on the nitrogen content of the original water gas. Until recently the methods technically developed for the removal of 2 to 4 per cent carbon monoxide have been operated at 100 atmospheres pressure or upward, generally at the working pressure of the ammonia synthesis operation. Such pressures are entirely unnecessary in technical hydrogenation and therefore involve unnecessary compression costs.

Operation of the carbon monoxide purification processes at lower pressures is less satisfactory. Hence the additional objections to these two processes of hydrogen manufacture for hydrogenation work. The chemical method of hydrogen production for the oil-hardening industry has therefore been what is variously known as the steam-iron process or the iron-contact process. It consists in the production of hydrogen by the interaction of steam and iron at temperatures in the neighborhood of 700 deg. C. The contact mass is regenerated by reduction of the iron oxide in a stream of a suitable reducing gas, normally water gas, whereupon the cycle of operations may be repeated. The hydrogen thus produced is easily obtained in a high state of purity. The gas can leave the producing system containing less than 1 per cent impurity, of which the bulk is carbon dioxide, easily removable, with but small fractions of 1 per cent of carbon monoxide and nitrogen. With special precautions these impurities can be diminished still further, even in the production process. As will be shown, also, newer methods of purification are capable of easy and cheap removal of carbon monoxide not in excess of 1 per cent, even in the presence of several per cent of carbon dioxide. The steam-iron process, therefore, without special refinement, is capable of yielding hydrogen of a purity sufficient for ammonia synthesis purposes.

The non-utilization of the steam-iron process in nitrogen fixation

work is to be attributed to three main factors: (*a*) the fuel cost, (*b*) the intermittency of the process and consequent high operating cost, and (*c*) the high cost of plant and of renewal of plant. These factors merit detailed consideration.

The fuel cost is high, since in the best practice hitherto attained in this process at least 2.5 volumes of water gas have been normally consumed in the production of 1 volume of hydrogen. The process at present, as regards fuel cost, ranks on a parity with the liquefaction process and is considerably inferior to the catalytic process. I have attempted elsewhere [3] to show that the high ratio of water gas consumed to hydrogen produced was to be attributed to the equilibrium relationships in the essential reactions of the process in both steaming and reducing phases. These reactions may be formulated by means of the following reversible equations:

$$3Fe + 3H_2O = 3FeO + 3H_2.$$
$$3FeO + H_2O = Fe_3O_4 + H_2.$$
$$3Fe + 3CO_2 = 3FeO + 3CO.$$
$$3FeO + CO_2 = Fe_3O_4 + CO.$$

Accepting the most recent and reliable data obtained by a single investigator covering these several equilibria,[4] I have computed the following tables of hydrogen and carbon monoxide consumption at equilibrium and the consequent water gas: hydrogen ratio deduced upon the assumption of such equilibrium conditions in the reducing phase.

Fe_3O_4-FeO Reaction

Temperature	Per Cent H_2 Consumed	Per Cent CO Consumed	Water Gas:H_2
570	27	47	2.7
650	41	55	2.1
750	58	67.5	1.6
850	75	75	1.33

FeO-Fe Reaction

Temperature	Per Cent H_2 Consumed	Per Cent CO Consumed	Water Gas:H_2
570	27	47	2.70
650	30	44	2.70
750	35	40	2.66
850	38	36	2.70

[3] "Industrial Hydrogen," A.C.S. Monograph; Chem. Catalog Co., 1921.
[4] Chadron, *Annales de Chimie*, 1921, vol. 16, p. 221.

From these figures it is evident that, assuming equilibrium, only by operating at high temperatures and on the Fe_3O_4-FeO cycle alone a ratio of water gas consumed to hydrogen produced equal to that yielded by the water gas catalytic process would be attained. The disadvantage of working on the Fe_3O_4-FeO cycle is made apparent by referring to the preceding equations, whence it is clear that only one-quarter of the output per unit of contact mass is obtained as compared with that yielded by the complete Fe_3O_4-Fe cycle.

Peculiar Conditions at the Start of Steaming and Reducing Periods

Recent investigations by Richardson, Vibrans, and Bell [5] on actual plant operations, as well as in laboratory trials, have shown that in the first minutes of either the reducing phase or, alternatively, of the steaming period, the conversion of the reacting gases is greater than that calculable from the above equilibrium figures or from any such data to which a degree of reliability can be assigned. It was found that the oxidation of the water gas to carbon dioxide and steam was much more nearly quantitative than the equilibrium figures would suggest. The implication of these results is that under conditions such as prevail in the first moments of the respective reactions it should be possible to obtain almost unit volume of hydrogen by the expenditure of a unit volume of water gas. For every molecule of water gas oxidized in the reducing phase a molecule of hydrogen accrues in the steaming phase. With such a water gas : hydrogen ratio, the steam-iron process is immediately on a parity with the catalytic process as regards fuel consumption. In addition, the gas purity and ease of purification of such hydrogen give to it a measure of importance worthy of serious consideration.

The explanation of the divergence between experimental results and theoretical equilibrium data is deserving of attention. At the moment, I incline to the view that complete consumption of the hydrogen and carbon monoxide of the water gas is approached in the early moments of the run, because in those moments the experimental conditions are such that the criteria for equilibria are not fulfilled. In any of the reactions involved, as, for example,

$$Fe_3O_4 + CO = 3FeO + CO_2,$$

it may readily be shown that, for a definite equilibrium ratio between

[5] A.C.S. Spring Meeting, Birmingham, Ala., 1922.

the two gases, it is demanded by the phase rule that *two* solid phases shall be present. At the outset of a run this condition is apparently not fulfilled; the gas in its travel through the retort system is then continually in contact with only one solid phase. At the beginning of the reducing phase this is the ferrous-ferric oxide Fe_3O_4. Only when the two solid phases Fe_3O_4 and FeO are present should the equilibrium be established. With only Fe_3O_4 present, oxidation of the carbon monoxide continues until either the carbon monoxide is completely converted to the dioxide or reduction of the ore is carried to the stage throughout the contact mass at which equilibrium relationships are possible.

The direction which development work in the steam-iron process should take is, therefore, obvious. Work should be directed toward devising working conditions such that the circumstances prevailing in the earlier moments of the process as at present conducted could be continuously maintained. The reorganization of the steam-iron process which such a study would involve would undoubtedly bring with it many improvements in the chemical engineering aspects of this industrial process, which hitherto has been left far too much in the hands of the empiricist, without attention from scientifically trained men. Diagrams of the multiple and single retort units as now operated are shown in Figures 3 and 4 respectively. In such a reorganization the intermittency of the process, which is quite unnecessary, could be eliminated. Operating costs should thereby be lowered. Cost of plant and of plant renewal would also receive attention. It is not too much to hope that the steam-iron process technologist would profit, in respect to plant and plant renewal, by the experiences of others in the matter of heat-resisting alloys and the economies resulting from their substitution for cast iron.

Given a steam-iron process so modified as to give a fuel : hydrogen ratio comparable with that now attainable in the water gas catalytic process, the advantages would all be with the steam-iron process. The expensive items in the water gas catalytic process are the purification processes. The removal of upward of 30 per cent carbon dioxide and a residual 2 to 4 per cent carbon monoxide is attained only at an expense somewhat greater than that involved in the production of the hydrogen-rich gas containing these impurities. Steam-iron process hydrogen, on the other hand, contains but 2 to 4 per cent total impurities, of which 1 to 2 per cent is carbon dioxide, 0.1 to 0.5

per cent carbon monoxide and residual sulphur compounds and nitrogen. The Harger-Terry process [6] of preferential combustion of carbon monoxide in hydrogen has solved the problem of purification of steam-iron process hydrogen satisfactorily and cheaply. It has now

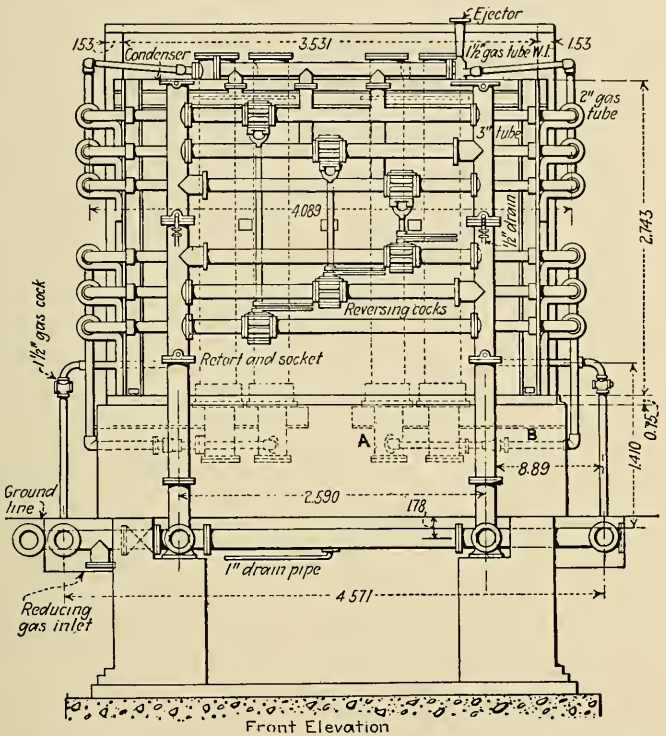


FIG. 3. Multiple Unit Retort for Steam-Iron Process for Hydrogen (From *Engineering*)

been operated successfully on a large technical scale in the United States. The process as now operated is applied to the gas leaving the iron oxide box system used to remove hydrogen sulphide from the gas issuing from the retorts. The sulphur-free gas so obtained is admixed with a small percentage of steam and oxygen sufficient to burn twice the theoretical quantity of carbon monoxide present. The mixture is raised to 200 deg. C. by a heat exchanger system and passed over a modified iron oxide catalyst containing suitable promoters at a

[6] Brit. Pat. 127,609 (1917); U. S. Pat. 1,366,176.

temperature within the interval 200 to 250 deg. C. In actual practice, on a technical scale a gas containing 0.5 per cent carbon monoxide has been purified so that less than 0.03 per cent of this impurity is left after the passage of the gas through the catalyst system. The

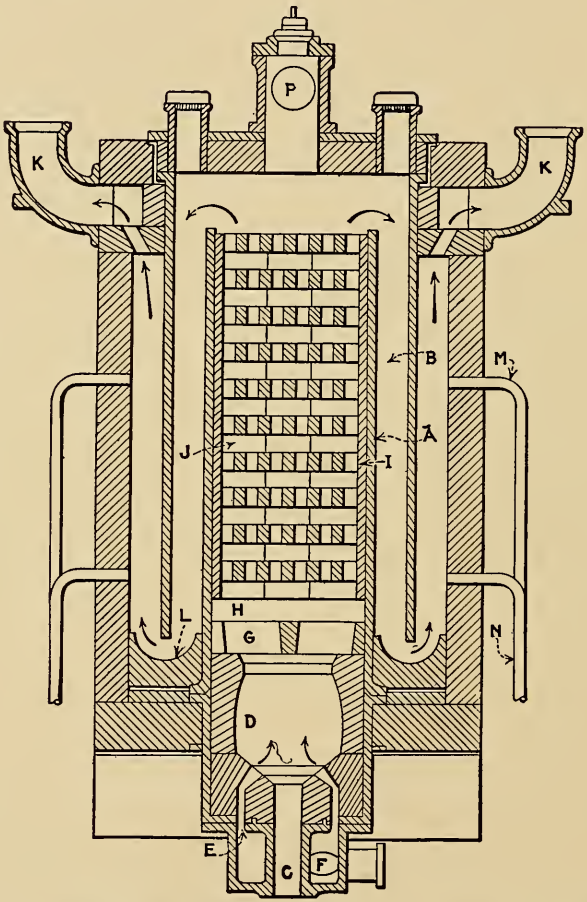


Fig. 4. Single Unit Retort for Steam-Iron Process for Hydrogen

carbon dioxide so produced, together with that originally present in the gases leaving the steam-iron process retorts, may be removed in the normal manner. In American practice this usually consists in scrubbing with caustic soda solution in coke-filled towers. In England lime boxes have been mainly used. The gases leaving such a

purification system are practically exclusively hydrogen, the impurities, with the exception of nitrogen (which also can, if desired, be kept quite low in concentration), never exceeding in such case more than a small fraction of 0.1 per cent. The product is therefore eminently suitable for ammonia synthesis purposes. A contrast of the purification process involved, carried out wholly at atmospheric pressure, at slight cost, with simple apparatus, with that involved with water gas catalytic process hydrogen, at once establishes its worth. Therefore, the steam-iron process still deserves the most thorough attention of the hydrogen technologist.

Electrolytic Hydrogen

At sources of cheap electrical power the electrolytic method of generating the gas will always be primarily considered. It is for this reason that in developments of ammonia synthesis in Norway electrolytic hydrogen is contemplated. This hydrogen is so pure that many of the problems of ammonia catalysis, bound up with the impurities in chemically prepared hydrogen, disappear. In such places as Norway power costs are relatively less important. Plant cost, however, represents still quite an item in the economy of the hydrogen production. In America even the electrical energy from water power is more costly than in Norway. Hence in America, even with water power, and more so with steam power, the electrolytic hydrogen industry for ammonia synthesis must meet competition from other types of hydrogen in both power costs and plant costs.

The electrolytic hydrogen problem must be considered as a hydrogen problem, as estimates of hydrogen costs based upon assumptions of a market for by-product oxygen will be fictitious. The by-product oxygen resulting from electrolytic production of the hydrogen will far exceed the extreme *present* oxygen-consuming capacity of any reasonable radius of industrial territory. It is necessary, therefore, to assume the oxygen wasted to the atmosphere.

The interdependence and variability of power charge, output, and capital cost of an electrolytic plant make a complete analysis of the problem difficult. An excellent effort in this direction has recently been made by Allan[7] based upon the use of off-peak power and of cells with higher than usual amperage. Allan predicates that in many hydro-electric plants off-peak power "could be sold for as low as one

[7] *Trans. Amer. Electrochem. Soc.*, Baltimore, Md., May, 1922. Preprint No. 10.

mill per kilowatt-hour and probably would not exceed 2.5 mills per kilowatt-hour under the most unfavorable conditions." For successful competition in ammonia synthesis the power costs must be within the above maximum.

The tendency toward high-amperage cells for higher operating efficiency at lower costs as indicated by Allan will certainly be followed in successful efforts to produce hydrogen for ammonia synthesis by the electrolytic method. Indeed, it may be stated that the figure quoted by Allan of 1,350 amperes as the normal current capacity of his cell will probably be greatly exceeded. During the war period experiments in the building of 10,000-ampere units were successfully engineered. It was found that a unit of such size could be operated with a voltage drop of 2.5 volts. With an overload, giving a cell operating at 15,000 amperes, a potential of 3 volts per unit was required. Wide flexibility of operating range with minimum variation in working efficiency will constitute an important factor in the design of such cells. It has been stated that the initial cost of such high amperage cells is not at all proportionate to that of the number of 500- to 1,000-ampere cells required to yield the same gas output. Hence a proportionate diminution in initial cost and therefore in interest, depreciation, wear and tear should result. Initiation of electrolytic manufacture of hydrogen for ammonia synthesis will constitute a bold experiment—if successful it will lead to industrial developments far outside the range of ammonia synthesis alone, by reason of the simultaneous oxygen production, uses for which would inevitably be sought.

Discussion

President Howard: This very interesting paper is open for discussion.

Dr. Bacon: I would like to ask what is the objection to the use of by-product hydrogen?

Dr. Taylor: There is no objection if it can be done economically. I think it can be done, but to undertake ammonia synthesis on a scale of tonnage of less than ten thousand tons per annum would not take one very far. Ammonia making has got to be done on the large scale or not at all. I don't think there is any future for such operations on a small scale, but it may be that in isolated communities it might be possible to put up a small plant which would supply local needs.

But I don't think there is any general future for the nitrogen industry in such small units. I think the main nitrogen fixation industry will be centralized in large units.

Mr. Thompson: In the case of steam-iron process hydrogen used in ammonia synthesis, how would the nitrogen be obtained economically?

Dr. Taylor: The nitrogen would be made either by liquefaction of air, as in Germany, or it could be made by a modification of the oxidization process. A certain amount of air would be run over the iron after the steam effect had taken place.

SOME ECONOMIC ASPECTS OF AMMONIA OXIDATION

Cost of Concentrating Weak Nitric Acid Produced by Ammonia Oxidation at Present More than Offsets Advantages Due to Lower Conversion and Nitrogen Costs—An Economic Study of the Factors that Determine when Ammonia Can Profitably Replace Saltpeter as a Source of Nitric Acid.

By GUY B. TAYLOR

Read at the Niagara Falls Meeting, June 19, 1922

If the primary product obtained by oxidizing ammonia were strong nitric acid, then ammonia on a price parity basis with Chilean saltpeter would be incomparably cheaper than saltpeter as a source for nitric acid. Unfortunately the primary product is nitric oxide and the cost of conversion of this oxide of nitrogen into strong nitric acid is considerable, in spite of the fact that the raw materials, water and air, required for doing so cost practically nothing. The industrial uses for weak nitric acid are so limited in extent that the oxidation of ammonia for the production of weak acid is of minor interest in the discussion. The question, then, of when it is economical to oxidize ammonia and when not to oxidize ammonia centers largely around the question of the cost of concentrating nitric acid. This state of affairs will continue as long as a small price differential exists between Chilean saltpeter nitrogen and ammonia nitrogen. With the development of processes for synthetic ammonia manufacture, the price differential is likely to change in favor of ammonia and the relative importance of nitric-acid concentration will vary as a factor in the situation.

The next most important factor, after raw materials cost and concentration cost, is the scale upon which manufacture is conducted. Nitric acid is an extremely corrosive liquid and on this account its transport is difficult and expensive. As a consequence nearly all large users manufacture at the place of consumption. Ammonia oxidation plants are not inexpensive to build and the first cost per ton of rated capacity is naturally greater the smaller the output. It might

pay to construct a new plant to produce nitric acid by oxidizing ammonia, while under a similar set of circumstances it would not pay to scrap a going retort process.

Comparison of Equipment and Manufacturing Processes

Before proceeding to more detailed comparisons, it is advisable to outline briefly the character of the plants required for the two processes. The essential units in the equipment are:

Ammonia Oxidation	Chilean Saltpeter
1. Ammonia liquor storage.	1. Soda storage.
2. Ammonia gas plant.	2. Sulphuric acid storage.
3. Ammonia converters.	3. Retorts.
4. Absorption system.	4. Condensers and receivers.
5. Nitric acid concentration.	5. Absorption system.

In the ammonia oxidation plant ammonia gas is distilled from liquor and mixed with air. The gas mixture is then put through a catalyst in the converter whereby nitric oxide and water vapor are produced. The gas then passes to the absorption system, where, coming in contact with water and air, the nitrogen oxides are converted to weak nitric acid with a strength of about 50 per cent. This weak acid is converted to 90+ per cent HNO_3 by distillation from sulphuric acid. This results in the production of weak sulphuric acid, from which the water must be boiled out in order that it may be used again.

In the saltpeter process sodium nitrate and sulphuric acid are charged into cast-iron retorts and strong nitric acid is distilled out and condensed. Toward the end of the distillation the distillate weakens somewhat due to thermal decomposition of HNO_3 and the release of water from the charge, previously held by the sulphuric acid. This weaker distillate is in some cases caught in a separate receiver and in others mixed with the strong distillate. Some nitrogen peroxide is evolved and recovered as dilute acid in the absorption system. The dilute absorption system acid and the weak distillate together seldom amount to more than 10 per cent of the yield.

In the ammonia oxidation process all of the output is recovered first as dilute acid, which must be concentrated, while in the saltpeter or retort process upward of 90 per cent of the output is directly recovered as strong acid. On the other hand, the retort process con-

sumes sulphuric acid in about equal tonnage with Chilean saltpeter and the ammonia-oxidation process consumes none.[1]

Fixed Charges—Construction and Operation

As a basis of comparing the two processes let us take a case favorable to ammonia oxidation. Let us assume that a new plant for nitric-acid manufacture is to be built in a locality favorable to large-scale production, say a place where 25,000 tons of HNO_3 per year can be disposed of. This is a convenient capacity rating to assume, because it approaches the largest conceivable peace-time production in any one place and because a plant of this size was actually built in this country during the war (U. S. Nitrate Plant No. 1). This gives us a line on probable plant cost. Such a plant will cost, say, $1,000,000, or $40 per ton-year. The first cost of a retort plant on this scale will amount to, let us say, $12 per ton-year, or less than one-third as much. The cost of operating the two plants will vary from time to time, but our estimate is that this cost will average about the same for each—that is, $10 per ton of product figured as 100 per cent HNO_3. This item, hereafter designated "operating cost," includes operating labor, repair labor, repair material and replacement, fuel and power, and superintendence. In the case of the ammonia oxidation process the operating cost of the concentration unit is excluded. The retort process requires about 1.4 tons of sulphuric acid per ton HNO_3. If this acid costs $16 per ton, the sulphuric acid cost per ton of HNO_3 will be about $20, making due allowance for niter cake credit.

In order to eliminate what may be termed the minor variables in the problem, let us assume the cost factors arrived at above are constants and study the major variables—nitrogen costs, yields and concentration costs. The assumed constants may then be summed up as follows and the sum designated "conversion cost":

	Ammonia Oxidation (As 50 Per Cent Acid)	Chilean Saltpeter (As 90+ Per Cent Acid)
Operating cost	$10	$10
Fixed charges at 15 per cent[2]	6	2
Sulphuric acid	0	20
Conversion cost, per ton of HNO_3	$16	$32

[1] Except the small quantity lost in repeated reconcentration of sulphuric acid required for dehydrating weak nitric acid.

[2] Includes the items of taxes, insurance, interest, amortization, and obsolescence.

Nitrogen Costs

In the chart shown in Fig. 1 the relations between the nitrogen costs of the raw materials and the finished product for various conversion efficiencies are presented graphically. The ordinate shows the cost of ammonia and sodium nitrate at parity in cents per pound

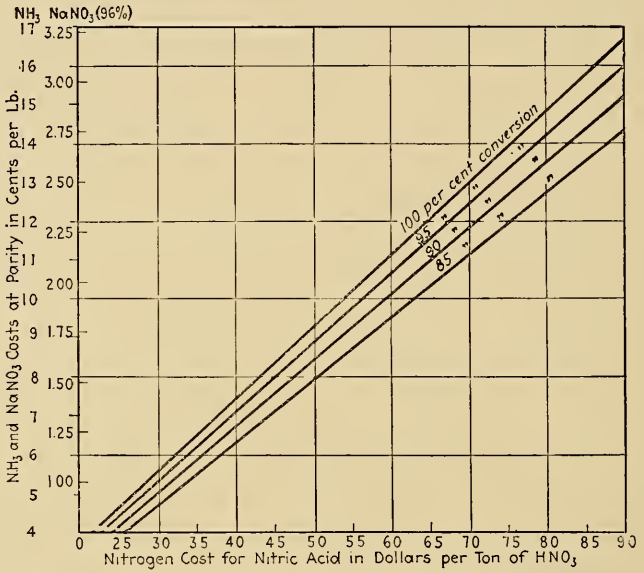


Fig. 1. Nitrogen Cost of Nitric Acid *vs.* the Cost of Ammonia and Sodium Nitrate for Various Conversion Efficiencies

and the abscissa the corresponding nitrogen cost for nitric acid in dollars per ton of HNO_3 at various conversion efficiencies. The nitrate is figured as 96 per cent pure.

The yield from nitrate may be conservatively put at 98 per cent and that from ammonia at 90 per cent (95 per cent oxidation efficiency and 95 per cent absorption efficiency). At these yields, with ammonia and nitrate at parity, and varying in price from 8c. to 15c. for NH_3 and 1.5c. to 2.9c. for nitrate, the total cost for nitric acid from ammonia varies from \$64 to \$106 per ton and for nitrate from \$76 to \$115 per ton. The spread between the two processes is only \$12 at the lower nitrogen cost and \$9 at the higher. That is to say, if 50 per cent nitric acid can be concentrated for much less than \$10 per ton, it pays to oxidize ammonia when ammonia and nitrate costs are on a parity basis.

The following tabulation gives a few examples of the spread between the two processes when nitrogen costs are not on a parity basis:

Cost of NH_3 Per Lb.	Cost of $NaNO_3$ Per Lb.	Ammonia Oxidation Cost of HNO_3 Per Ton (50 Per Cent)	Chilean Saltpeter Cost of HNO_3 Per Ton (90+ Per Cent)
8c.	1.75c.	$64	$ 82
10	2.25	76	97
12	2.50	88	103
12.5	2.25	91	97

The first three cases in the above tabulation are taken at prices showing not unusual disparities in price quotations between ammonia and nitrate, and in favor of ammonia. In the last case, ammonia is relatively the higher priced and is about the condition of affairs that obtained in the early months of this year. From the above it will be observed that ammonia as a source of weak nitric acid is cheaper than saltpeter at any disparity in nitrogen cost that is likely to occur.

It is doubtful whether the over-all yield of an ammonia oxidation plant can ever closely approach the efficiency of the retort process, which in well-conducted works averages 98 to 99 per cent. The catalytic oxidation efficiency to be expected under the best conditions can scarcely be more than 95 per cent and absorption efficiency 98 per cent, or an over-all of 93 per cent. On a nitrogen parity, then, nitrogen for the ammonia oxidation plant must always cost more, but this is more than balanced by sulphuric acid used in the retort process. As a matter of fact, based on prices in normal years, the nitrogen costs of the two processes would have been about the same in the past, because ammonia commanded a less price per pound of nitrogen than did nitrate. The thing to be emphasized in considering yield is the relative importance of yield gains to any probable operating economies. An addition of 1 per cent to the yield means more in dollars and cents than a reduction of 10 per cent in operation cost or fixed charges.

Costs of Concentration

The concentration cost, the most important item under present conditions militating against any widespread adoption of ammonia oxidation, is a difficult matter to estimate. Nitric acid has never been concentrated in this country on the scale assumed in our comparisons,

except under war conditions. The cost of this operation will probably lie between $20 and $40 per ton of HNO_3. Assuming that it can be done for the lower figure, what price can we afford to pay for ammonia in order to compete with Chilean saltpeter? In the following tabulation the first column shows an assumed price for saltpeter, the second column the corresponding cost of ammonia at parity, the third column the price to which ammonia would have to fall to break even with saltpeter, and the fourth the estimated cost of nitric acid at the break-even condition. Yield from nitrate is taken at 98 per cent and from ammonia at 90 per cent. The conversion cost of ammonia is taken at $16 and of nitrate $32 per ton HNO_3; $20 is added to the ammonia oxidation process for concentration.

Cost of Chilean Saltpeter, Cents Per Lb.	Cost of Ammonia		Cost of HNO_3 Dollars Per Ton
	At Parity, Cents Per Lb.	Competing Price, Cents Per Lb.	
2.0	10.5	8.8	89.00
2.5	13.0	11.2	103.50
3.0	15.6	13.7	118.00

The above tabulation shows that ammonia must be obtainable for at least 2c. per lb. less than the parity price in order to show any considerable saving over Chilean saltpeter at 2c. to 3c. per lb. as a source for strong nitric acid.

Improvements in the Ammonia Oxidation Process

The catalytic oxidation of ammonia gas to nitric oxide—that is, the ammonia-conversion step in the process—may be considered as in a very satisfactory state. Obviously, from what has been said above, the point of attack in improving the process is to solve the problem of more cheaply converting nitrogen oxides to concentrated nitric acid. Seventy per cent of the plant cost is swallowed up in huge absorption towers recovering weak acid. And this weak acid must be concentrated. This problem in connection with the arc process, in which these features are greatly magnified, has received much attention abroad, as witnessed by an extensive patent literature. But not one of these proposals looks promising even on paper, and needless to say none has ever reached the commercial stage of development.

Conclusions

All things considered, it may be concluded as a result of this study that under present conditions, as a source for strong nitric acid, saltpeter has a slight advantage over ammonia. The conversion cost and the nitrogen cost (usually) of ammonia are less than corresponding costs of sodium nitrate, but this advantage is more than offset by the necessity for concentrating nitric acid in the ammonia process. The advantage of the retort process probably increases as the scale of manufacture decreases. If the price of ammonia falls, as is likely with the coming into production of synthetic ammonia plants on a large scale, then the slight advantage of the retort process will disappear. It is conceivable that the time may come when it will no longer pay to import Chilean saltpeter at all as a source of nitric acid.[3]

There are two uses for which ammonia oxidation may be profitably employed immediately. In the writer's opinion all lead chamber or "nitration" sulphuric acid plants should be equipped with ammonia converters. In this case the plant investment is relatively small. The nitrogen oxides are used as such, no absorption system of any kind being needed. The ease of control and uniformity of supply ought to be of considerable advantage to the sulphuric acid plant operation. The second possible immediate use for ammonia oxidation is for the production of weak nitric acid. There are a few industries utilizing weak acid, having no use for strong acid. If the requirements are sufficiently large, it would pay to oxidize ammonia.

Experimental Station,
E. I. du Pont de Nemours & Co.

Discussion

President Howard: This paper is open for discussion.

Dr. Reese: That paper confirms the contention that I have always made that it would not pay to make nitric acid out of ammonia, because ammonia has practically the same nitrogen value as nitrogen of soda. The great difficulty, as pointed out in the paper, in attempting to manufacture nitric acid from ammonia is that it involves a very large capital expenditure, and the reason that it has not been done to any extent except for war purposes is that by a slight change in the

[3] In this connection it should be remembered that the export duty on Chilean saltpeter from Chile is a considerable fraction of its total cost. This tax will no doubt be reduced to meet competition with ammonia, should the market for saltpeter be seriously threatened.

export duty or reduction in the cost of soda your entire investment might be wiped out. That is a very serious objection to a large investment for the manufacture of nitric acid from ammonia.

MR. BACON: A parallel difficulty also comes in there in the varying price of freight. I assume that the freight in this country is a larger item than the export duty.

DR. REESE: It is rather interesting also from the point of view of the Naval Consulting Board, whose meetings I attended during the war, when the tendency was all along the line to go into oxidation of ammonia for nitric acid manufacture, and at that time my feeling was that the cost of oxidation was really too high. Cheap power is good for both sides, just as Dr. Taylor has shown in his discussions of the ideal method of producing hydrogen for ammonia, but the tendency of the Naval Board during the war was all for oxidation of ammonia, which resulted in the building of that white elephant down in Alabama at Muscle Shoals.

CONCENTRATING DILUTE NITRIC ACID SOLUTIONS

A Study of Rate of Concentration—Application of Results to Fractionation—Determination of Composition of Vapor Above Boiling Solution of Known Composition

By CLIFFORD D. CARPENTER and JOSEPH BABOR

Read at the Niagara Falls Meeting, June 19, 1922

The problem of concentrating dilute solutions of nitric acid may be conveniently divided into two stages, preconcentrating and superconcentrating—i.e., bringing the acid up to 50 or 60 per cent by simple fractionation and making acids of higher concentration which requires some special process.

This report will deal only with the problem of preconcentrating. Work is in progress on the problem of superconcentrating and the results will be reported at a later time. For our own convenience in describing our work and discussing the application of the results, we will divide the report into two parts. The first will give our results and discuss them in relation to concentrating the dilute acid by simple distillation and by fractionation.

Part I.—Analytical Methods Used

In a recent article[1] we described a method by which we were able to distil a solution in such a manner as to prevent all errors introduced by fractionation and therefore study the rate of change in the concentration of the boiling solution while removing a vapor which was continuously in equilibrium with the boiling solution. While making more extended experiments we found ourselves in trouble on duplicating our results. We found our method of standardizing the base (succinic acid) was not easily duplicated, so we tried the thallate and benzoic acid methods, which checked each other, but did not check the value given by the succinic acid method. We then secured from the Bureau of Standards a sample of benzoic acid with which the base used in these experiments was standardized. We have made a much more extended study of the problem using the experimental procedure described in our first article.

[1] *Chem. Met. Eng.*, 26, 443-4 (1922).

The Tables I to VI give the results obtained and Fig. 1 gives these results expressed graphically. The upper curve of Fig. 2 is a composite expression for the rate of change in the concentration of 1,000 grams of a 5 per cent acid from 5 to 68 per cent. The points which

TABLE I

RATE OF CONCENTRATING OF NITRIC ACID FROM 3.34 TO 39.97 PER CENT
Barometer 762.15 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
712.516	0.0	0.0	0.0	3.34
631.23	81.29	0.0275	11.41	3.77
554.10	158.42	0.0576	22.23	4.29
474.20	238.31	0.0907	33.45	5.00
391.90	320.62	0.1379	45.00	6.04
317.36	395.16	0.1953	55.46	7.44
245.29	467.23	0.2813	65.58	9.59
178.03	534.49	0.4240	75.02	13.10
131.69	580.83	0.6906	81.52	17.56
77.14	635.38	1.6730	89.18	28.70
50.72	661.79	3.5215	92.88	39.97

TABLE II

RATE OF CONCENTRATING NITRIC ACID FROM 11.73 TO 65.13 PER CENT
Barometer 756 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
545.802	0.0	0.0	0.0	11.73
493.66	52.14	0.211	9.55	12.92
444.26	101.54	0.439	18.60	14.31
386.69	159.11	0.764	29.15	16.35
327.09	218.71	1.236	40.07	19.19
266.19	279.60	2.050	51.23	23.28
211.25	334.55	3.441	61.30	28.67
164.97	380.83	5.803	69.77	35.28
117.114	428.69	11.298	78.54	45.01
64.315	481.49	26.424	88.22	58.44
33.48	512.32	42.169	93.87	65.13

TABLE III

RATE OF CONCENTRATING OF NITRIC ACID FROM 21.08 TO 62.43 PER CENT
Barometer 765 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
718.127	0.0	0.0	0.0	21.08
657.62	60.51	0.93	8.43	23.35
588.10	130.03	2.34	18.11	25.34
514.32	203.81	4.52	28.38	28.56
443.15	274.98	7.60	38.29	32.44
357.82	360.31	14.30	50.18	38.30
270.94	447.18	27.33	62.27	45.77
187.17	530.96	49.26	73.95	54.55
105.26	612.86	85.65	85.32	62.43

TABLE IV

RATE OF CONCENTRATING NITRIC ACID FROM 34.24 TO 63.44 PER CENT
Barometer 766.7 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
728.196	0.0	0.0	0.0	34.24
649.74	78.46	6.357	10.77	37.43
562.85	165.35	16.14	22.71	41.47
476.80	251.39	30.06	34.52	46.03
385.36	342.84	51.73	47.19	51.33
302.76	425.44	79.25	58.43	56.25
216.10	512.10	117.80	70.31	60.96
165.07	563.13	144.83	79.13	63.44

TABLE V

RATE OF CONCENTRATING NITRIC ACID FROM 51.74 TO 66.93 PER CENT
Barometer 755 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
618.093	0.0	0.0	0.0	51.74
533.420	84.67	27.73	13.70	54.76
446.44	171.66	61.670	27.77	57.83
364.70	253.39	99.160	41.00	60.50
294.43	323.67	135.560	52.37	62.58
218.45	399.64	178.810	64.66	64.55
157.62	460.47	215.935	74.50	65.91
96.68	521.42	255.110	84.36	66.93

TABLE VI

RATE OF CONCENTRATING OF NITRIC ACID FROM 59.75 TO 67.16 PER CENT
Barometer 758.0 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent
584.87	0.0	0.0	0.0	59.75
537.20	47.67	23.11	8.15	60.75
480.94	103.93	51.61	17.77	61.94
475.86	109.01	54.28	18.64	62.04
417.08	167.79	86.06	28.69	63.16
350.59	234.28	124.22	40.06	64.26
296.38	288.49	156.48	49.33	65.13
244.87	340.00	188.23	58.13	65.86
184.95	399.92	226.52	68.38	66.49
122.32	462.55	267.48	79.08	67.05
89.51	495.36	289.38	84.70	67.16

define this line are obtained from the results given in the six tables and are given in Table VII. The lower curve in Fig. 2 is a composite expression for the rate, in grams, at which the same acid escapes in the vapor while the concentration of the boiling acid changes from 5 to 68 per cent. If we read the points, in terms of the left-hand ordinate, at which the upper curve intersects the vertical lines representing the composition of the boiling solution, we have the amount of distillate. If we read the points, in terms of the right-hand ordinate, at which the same line intersects the lower curve, we have the amount of acid which is in the distillate. These points give the results in Table VIII.

An examination of Figs. 1 and 2 shows that very little acid is lost in the distillate until the concentration of the boiling solution reaches 20 per cent (1.6 g. acid to 759 g. distillate). The rate of loss increases slowly until about 30 per cent (2.4 g. acid to 809 g. distillate), when the rate becomes much greater, but remains rather regular until about 55 per cent, when it again begins to increase more rapidly. At 63 or 64 per cent there seems to be a striking change and the concentration of the vapor approaches that of the residue very rapidly. It is possible that the peculiar inflexion in the curve between 63 and 64 per cent can be accounted for by assuming the presence of $2H_2O \cdot HNO_3$. The curve shows that the rate of change is regular enough to permit efficient fractionation up to a 55 or 60 per cent acid.

TABLE VII

VALUES CALCULATED FROM VALUES IN TABLES I TO VI BY WHICH THE POINTS OF THE COMPOSITE CURVES IN FIG. 2 ARE DEFINED

From Table I			From Table II			From Table III			From Table IV			From Table V			From Table VI		
Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams	Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams	Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams	Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams	Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams	Strength of Boiling Acid, Per Cent	Weight of Distillate, Grams	Weight of Acid In Distillate, Grams
5.0	0.0	0.0	11.73	580.0	0.58	21.08	770.00	1.78	34.24	867.50	4.70	51.74	932.00	14.70	59.75	956.0	23.70
6.0	173.8	0.11	12.92	620.12	0.75	23.03	789.38	2.08	37.43	881.78	5.86	54.76	941.31	17.75	60.75	959.6	25.44
7.44	331.0	0.23	14.31	658.30	0.93	25.34	811.63	2.53	41.47	897.59	7.64	57.83	950.89	21.48	61.94	963.8	27.58
9.59	482.75	0.41	16.35	702.40	1.18	28.56	835.25	3.22	46.03	913.21	10.17	60.50	959.88	25.61	62.04	964.2	27.78
13.10	625.0	0.76	19.19	748.3	1.54	32.44	858.02	4.21	51.33	930.02	14.11	62.58	967.61	29.61	63.16	968.2	30.17
17.560	722.7	1.28	23.28	795.2	2.16	38.30	885.35	6.36	56.25	944.93	19.12	64.55	975.96	34.38	64.26	973.6	33.05
28.7	837.0	3.35	28.67	837.5	3.23	45.77	913.20	10.53	60.96	960.69	26.13	65.91	982.66	38.45	65.13	977.7	35.47
39.97	892.7	7.20	35.28	873.0	5.05	54.55	940.10	17.55	63.44	972.40	31.06	66.93	988.67	42.76	65.86	981.6	37.86
			45.01	909.8	9.28	62.43	966.10	29.18							66.49	986.1	40.70
			58.44	950.5	20.91										67.05	990.8	43.82
			65.13	974.2	33.03										67.16	993.3	45.47

TABLE VIII

INTERPRETATION OF FIG. 2

Change in Composition of Boiling Solution from 5 per cent to	Grams of Distillate	Grams Acid In Distillate	Change in Composition of Boiling Solution from 5 per cent to	Grams of Distillate	Grams Acid In Distillate
10 per cent	505.0	0.5	40 per cent	892.5	7.07
15 per cent	670.0	0.95	45 per cent	910.0	9.75
20 per cent	758.0	1.60	50 per cent	926.5	13.25
25 per cent	810.0	2.40	55 per cent	941.3	17.75
30 per cent	845.0	3.55	60 per cent	956.7	24.10
35 per cent	871.5	5.05	65 per cent	977.0	35.20

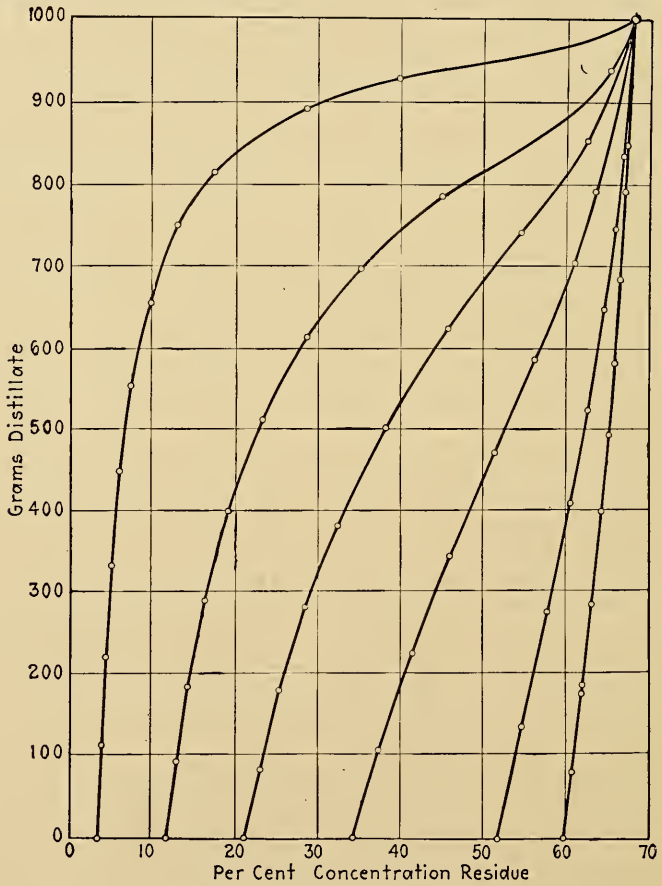


FIG. 1

Galle [2] recently studied the preconcentration of nitric acid by using a flask to which was sealed a fractionating column, and as a result of his experiments advises the fractionation of dilute acid solutions up to 65 per cent before employing methods for superconcentrating the acid. It is evident, however, that the efficiency of fractionation will be much less above a 55 to 60 per cent composition.

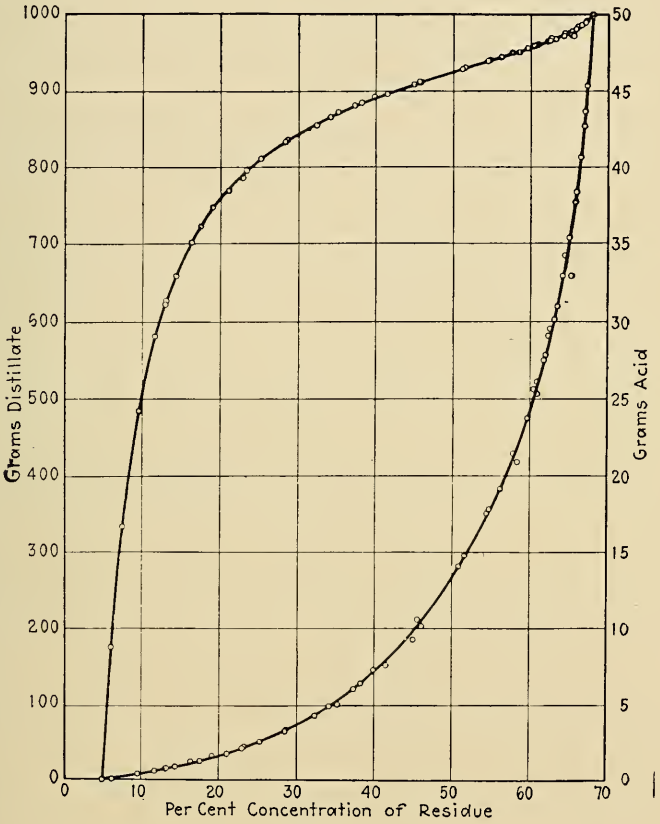


FIG. 2

If we wish to obtain a 55 per cent acid from 1,000 g. of a 20 per cent acid by simple distillation, the first residue will be 242.6 g., containing 133.4 g. of the original 200 g. of acid. The first distillate of 757.4 g. will contain the other 66.6 g. of acid and will have a com-

[2] *Z. Angew. Chem.*, 1921, vol. 34, pp. 168 to 170; 173 to 175.

position of about 8.8 per cent acid. A distillation of the first distillate will produce 78.7 g. of a 55 per cent acid containing 43.3 g. of acid and give a second distillate of 678.7 g. with a composition of about 3.4 per cent. This means by two distillations requiring the vaporization of 1,336 g. of dilute acid that 321.3 g. of 55 per cent acid can be obtained from 1,000 g. of 20 per cent acid, a recovery of about 177 g. or nearly 90 per cent of the 200 g. of acid in the original 20 per cent solution. If a third distillation is made, about 15 g. more of acid may be recovered as 55 per cent acid and about 650 g. of 1 per cent distillate removed. This means that in three fractionations requiring the vaporization of about 1,985 g. of dilute acid that about 92 per cent of the original acid may be recovered as 55 per cent acid.

If it were desired to obtain a 65 per cent acid from the 20 per cent acid, the first distillate removed would be 905 g. containing 138.25 g. of acid, while there would remain 95 g. of 65 per cent acid. The second distillation would begin with 905 g. of little more than 15 per cent acid and would require the removal of 840 g. of distillate, leaving 65 g. more of 65 per cent acid. Two distillations of a 20 per cent acid will give 160 g. of 65 per cent acid by vaporizing, 1,745 g. of dilute acid. This means a recovery of 104 g. of the original 200 g. of acid. In order to recover 90 per cent of the acid from a 20 per cent solution as 65 per cent acid, many fractionations would be required.

From our data it becomes a simple matter to calculate the number of fractionations required to recover nitric acid from dilute solutions at a higher concentration.

Part II.—Composition of the Vapor

If we take the curves given in Figs. 1 and 2 and plot them on large co-ordinate paper, it will be quite easy to read the amount of distillate and the amount of acid in the distillate while the strength of the acid changes 1 per cent from any desired concentration to the next higher. Knowing from the data given in Tables I to VI the rate at which the distillate is increasing, a very close estimate can be made for the composition of the vapor of the boiling solution at a concentration represented by the mean composition. Such calculations have been made by reading the values from the curves and the results are given in columns headed C and B in Table IX, and have been used to define the curve given in Fig. 4.

Recently Pascal[3] and Berl and Samtleben[4] have carried out experiments in order to determine the composition of vapor above a boiling solution of nitric acid of known concentration. Both used an air bath heated by means of a Bunsen burner. They inclosed the flask containing the boiling liquid in the air bath in order to prevent con-

TABLE IX

COMPARISON OF VALUES GIVEN FOR THE VAPOR COMPOSITION ABOVE BOILING NITRIC ACID SOLUTION

Strength of Acid	Strength of Vapor			Strength of Acid	Strength of Vapor		
	Carpenter and Babor	Berl and Samtleben	Pascal		Carpenter and Babor	Berl and Samtleben	Pascal
5.00	0.048	....	....	45.00	18.00	....	....
10.00	0.200	....	....	47.50	22.20	....	....
12.50	0.35	....	....	47.77	....	21.71	....
13.45	.....	0.46	....	49.80	....	....	19.85
15.00	0.55	....	....	50.00	26.50	....	....
17.50	0.75	....	....	52.50	31.10	....	....
20.00	1.05	....	....	53.96	....	33.51	....
20.58	.....	1.26	....	55.00	35.50	....	....
22.50	1.45	....	....	56.60	....	39.37	....
24.20	.....	....	2.16	57.50	41.70	....	....
25.00	2.20	....	....	60.00	47.80	....	50.02
27.50	3.00	....	....	61.47	....	51.34	....
30.00	4.10	....	....	62.50	54.60	....	....
31.75	.....	4.94	....	62.64	....	54.46	....
32.50	5.60	....	....	65.00	60.80	....	....
33.00	.....	....	5.90	65.18	....	60.62	....
35.00	7.30	....	....	67.43	....	65.97	....
37.50	9.40	....	....	67.10	66.80	....	....
37.99	.....	9.20	....	67.89	....	67.84	....
40.00	12.00	....	....	68.00	(68.00)	68.00	....
42.50	14.90	....	....	68.40	....	....	68.40
43.50	.....	14.86	....				

densation in the upper part of the flask and delivery tube. Fig. 3a, gives a sketch of our apparatus, described in our recent paper,[1] and the ones used by those referred to above. In the case of Pascal, Fig. 3b, two thermometers are suspended, while Berl and Samtleben, Fig. 3c, used only one. We have left out the thermometer, as it would act as a fractionation column. The only way in which heat can be transmitted to it is by conductance from the boiling liquid and

[3] *Ann. Chim.*, 1921. New series, vol. 15, pp. 253 to 290.

[4] *Z. Angew. Chem.*, 1922, vol. 35, p. 201.

through the vapor. This fractionating effect would be very small in the more dilute solutions, but as the concentration increases such an error becomes more serious, especially at the points where the change is most rapid. In our method it would be very serious, for any such error becomes cumulative. If, however, it is only desired to know the composition of a vapor above a boiling acid, the error due to fractionation on a thermometer could be made negligible compared with the experimental accuracy possible by taking a small fraction from a large amount of boiling acid. Berl and Samtleben did this and their results are given in the second column in Table IX and are indicated in Fig. 4 by circles to which are attached small arrows. Those falling directly on our curve are indicated by two arrows, and those falling to one side by one arrow pointing in the direction indicating the side upon which the point falls. They have made a slight

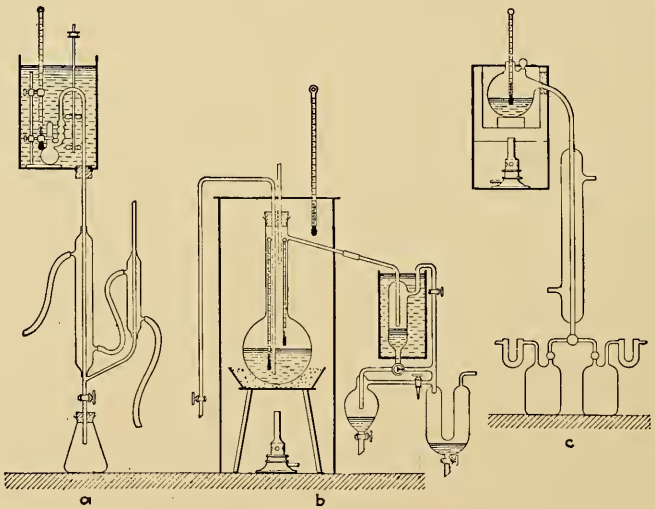


FIG. 3

error in their estimation of the composition of the vapor, however, for they assume the concentration of the distillate to be the composition of the vapor above a boiling acid which is the mean between the composition of the boiling acid at the beginning and at the end of the change which takes place while the distillate is being collected. It is evident from the shape of the curve in Fig. 2 that this could only be approximately true for the lower concentrations of acids. They have

partly corrected the error in this assumption by taking small fractions in the higher concentrations, which, of course, results in a larger experimental error in determining the amount of acid in a small fraction.

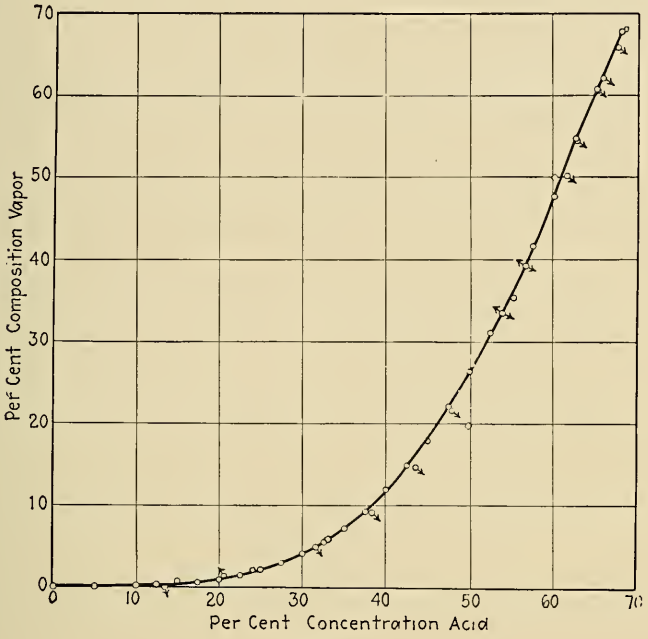


FIG. 4

Take, for example, their values obtained for 31.75 per cent (obtained by assuming the concentration of the distillate, 4.94 per cent, while the boiling acid changes from 30.22 per cent to 33.28 per cent to be the composition of the vapor of the mean concentration 31.75 per cent), for 37.99 per cent (residue changing from 37.13 to 38.85 per cent, the distillate of which was 9.20 per cent acid), for 43.50 per cent (residue changing from 42.73 to 44.27 per cent, the distillate of which was 14.86 per cent), and for 47.77 per cent (residue changing from 45.57 to 49.96 per cent, the distillate of which was 21.71 per cent), and note their position in Fig. 4. These values all fall to the right of the curve, for in this range the concentration is changing rapidly and the composition of the distillate represents the composition of the vapor for a lower concentration of boiling acid than obtained by taking a mean value. While the values are in close agreement with

those given by us, most of the points fall to the right of our curve as would be expected.

Pascal has given the values obtained for five points. They are given in column headed P in Table IX, and indicated in Fig. 4 by small squares.

Conclusion

1. All values given in our first paper have been redetermined.

2. A brief discussion of the use of our results in considering the problem of fractional distillation has been given.

3. The composition of the vapor above a boiling nitric acid solution from 5 per cent to 68 per cent composition has been determined.

4. A comparison has been made between our results and those obtained by Berl and Samtleben and by Pascal, and errors in their methods have been indicated.

5. When the rate at which the distillate is removed while the change in the concentration of a boiling acid solution is known, it becomes a very simple matter to calculate the amount of distillate necessary to be removed by successive distillations in order to recover any desired amount of the acid at a higher concentration.

Discussion

Dr. Carpenter: When we first planned to discuss this problem we expected only to extend our experimental work described in a previous paper in the March issue of the *Chemical and Metallurgical Engineering Journal.* While this new work was being carried out it soon became apparent that the published results were consistently too low. After an investigation into the causes, it was discovered that the succinic acid used by us in standardizing our base was not reliable. We then obtained from the Bureau of Standards some benzoic acid which has been used as the standard for the results given in this paper. Although the first paper gave some results, it was presented as a method for studying distillations by which the vapor phase could be kept in equilibrium with the liquid phase without danger of fractionation. We have, therefore, used the method to repeat the earlier experiments and to extend them, in order to obtain results, as a basis for the discussion of the preconcentrating of dilute nitric acid. The problem of superconcentrating nitric acid is being studied and will be reported in a later paper. Although we have

studied this problem as a laboratory experiment, there is no reason why the conditions should not obtain in an efficient fractionating column in an industrial operation.

MR. ZEISBERG: I might say a lot about the inaccuracies of the Pascal data. I made calculations extending over many months on the basis of Pascal's results, and then found that Pascal's graphs do not agree with his figures. Dr. Carpenter has shown that Berl and Samtleben's results are close enough for all practical purposes, and I am inclined to think that those results are the ones I should have used, and now I have about three months' work to do over again. I should like to commend Dr. Carpenter's work, which is very important and doubtless the most accurate work so far done on this subject. It is quite possible to determine from his curve what separating effect can be obtained in a nitric acid fractionating column and predict accurately what height of column is necessary. Consequently this work is exceedingly valuable.

THE AIR BLEACHING OF NITRIC ACID

An Experimental Study of the Bleaching of Nitric Acid with Air—Effect of Temperature, Air Velocity, Etc., Discussed and Analyzed—A Formula is Derived for Calculating the Bleaching Coefficient which is Checked by Experiment.

By W. G. WHITMAN and LAIGHTON EVANS

School of Chemical Engineering Practice

Massachusetts Institute of Technology

Read at the Niagara Falls Meeting, June 21, 1922

The problem of bleaching nitric acid to be used in the manufacture of mixed acid has assumed greater importance as the specifications on lower oxide content have become more rigid. This has stimulated the development of better methods of operating and controlling the bleaching process which is necessary in the older types of plants. This paper presents the results of experimental work on bleaching nitric acid at varying temperatures and air rates, and develops a theory and an equation whereby these results can be applied to industrial practice.

Removal of Lower Oxides.—The process of bleaching strong nitric acid with air consists essentially of volatilizing the lower oxides present and removing them by the current of air. There are, therefore, three important factors involved. In the first place, the vapor pressure of the lower oxides, determined by their concentration and the temperature of the solution, is a direct measure of their tendency to volatilize. Next, a source of heat is necessary to supply the heat of vaporization. Finally, the volatilized oxides must be removed from the system—a process which is effected in this case by a current of air. These three factors will be discussed separately.

First Factor: Vapor Pressure of Lower Oxides.—Owing to the relatively low concentration, the vapor pressure of the lower oxides at any given temperature may be assumed to be directly proportional to their concentration in the solution (Henry's Law)—i.e., $p = aN$

where p = the partial pressure of lower oxides, N = the concentration of lower oxides in the solution (expressed as per cent N_2O_3), and α = the proportionality constant. It is obvious that α will vary with the temperature of the solution, and, by analogy with other cases, an exponential function may be predicted.

Second Factor: Heat of Volatilization.—The major source of heat is the solution itself, which cools during the bleaching process. It is, of course, possible to supply heat externally and prevent cooling, but this does not alter the concept. It is impracticable to supply much heat in the air used for bleaching, since the sensible heat of the air stream is necessarily small compared to the total heat required for evaporation.

Third Factor: Mechanical Removal of Vaporized Oxides.—The air used to remove the volatilized products could theoretically become saturated in an ideal bleaching pot. Actually, this condition is nearly realized, so that an approximation that the air reaches the same percentage saturation under different conditions of temperature and velocity is justified. The oxide removal should, therefore, be nearly proportional to the air rate, varying only by slight differences in the saturation of lower oxides at different air velocities.

The bleaching formula derived from these considerations is as follows:

$$-\frac{dN}{d\theta} = \beta N,$$

where N = per cent N_2O_3 in solution,

θ = time in minutes,

β = the bleaching coefficient, defined as the drop in per cent lower oxides per minute in a 1 per cent solution,

$-\frac{dN}{d\theta}$ = the instantaneous rate of bleaching.

The above equation states that the rate of removal of the lower oxides is a function of the amount of oxides present. This equation integrates to the form

$$\log_e N = -\beta\theta + \text{constant}$$

or between the limits of an initial concentration N_1 and a final concentration N_2

$$\log_e \frac{N_2}{N_1} = -\beta(\theta_2 - \theta_1).$$

The coefficient β is not a constant, but varies with the temperature of the solution and the air rate, and should be nearly proportional to the latter. All laboratory runs were made with constant temperature and air rate, so that β was itself constant for any one run. It is obvious that the validity of the theory and assumptions given above must be demonstrated by comparing the equation to actual data obtained in bleaching runs.

The absence of data on the vapor pressure of lower oxides has made it impossible previously to calculate the rate of bleaching. In this work it has been considered that the actual vapor pressure obtained from laboratory bleaching runs is the vapor pressure of oxides above the solution. This is not strictly true, since, as noted previously, the air does not become saturated. However, the approximation that the same degree of saturation is reached in all cases permits this assumption, and, furthermore, such vapor pressure data are applicable to other bleaching runs in which complete saturation is again unattainable.

Loss of Nitric Acid.—During the removal of lower oxides, nitric acid will itself be volatilized, but the problem is somewhat simplified in that the vapor pressure of nitric acid remains constant during a run at any one temperature, since the amount vaporized is so small. Although data on the vapor pressures of HNO_3 in concentrated solutions at higher temperatures are a little uncertain, it is possible to calculate the values from data at lower temperatures using the Clapeyron equation. These values may be compared with observed values.

The experimental work consisted in bleaching nitric acid on a laboratory scale under various conditions of temperature and air rate. Compressed air was passed through a calibrated flow meter and then to a 2-liter bleaching flask, where it was distributed in the acid by a perforated glass coil. The flask was equipped with a thermometer, a gas burner for heating, and an exhaust tube for the gases, which also acted as an air-cooled condenser. The amount of nitric acid lost during the process by evaporation was measured by collecting the condensate.

Each test consisted of bleaching 1.5 liters of raw acid (93 per cent HNO_3) at a definite temperature and air rate. At intervals during the bleach acid samples were siphoned from the flask and analyzed for dissolved lower oxides of nitrogen by titrating a diluted

sample with tenth normal $KMnO_4$; the oxides being expressed as N_2O_3. Approximately 200 c.c. of the acid was removed as samples, giving an average volume of 1.4 liters.

The first set of three runs was made at constant air rate, equal to 0.66 liter air per minute per liter of acid, and temperatures of 60, 65, and 70 deg. C., respectively. Air rate is expressed as the ratio of air volume per minute per unit volume of acid, so that the results would be comparable with plant practice. The second set of three runs was made at constant temperature—namely, 70 deg. C.—and air rates of 0.51, 0.66, and 0.75 liter per minute per liter of HNO_3, respectively.

If the original equation $\log_e N = -\beta\theta + \text{constant}$ is true, then plotting $\log_e N$ against β should give a straight line whose slope equals $-\beta$.

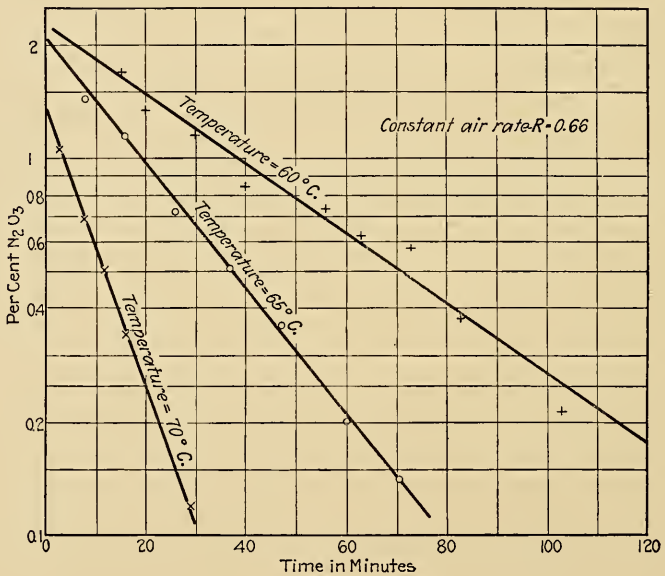


FIG. 1

Fig. 1 shows log of the lower oxide concentration plotted against the time of bleaching for runs at three different temperatures, but at a constant air rate. The points for a given run all fall close to a straight line, thus verifying the original law for rate of bleaching. Fig. 2 shows the log of the lower oxide concentration also plotted

against time of bleaching for runs at three different air rates, but at a constant temperature. These points for a given run, all falling close to a straight line, again verify the original equation.

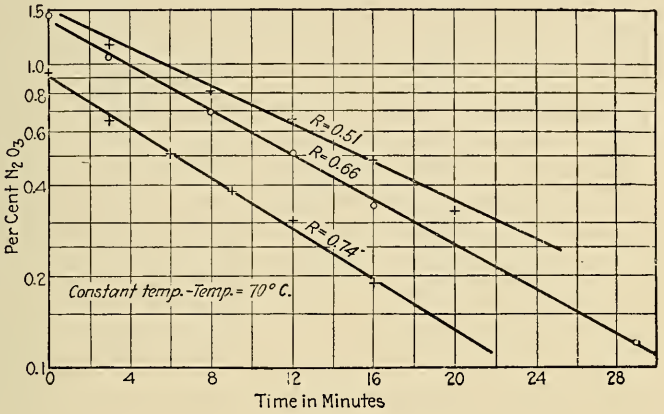


FIG. 2

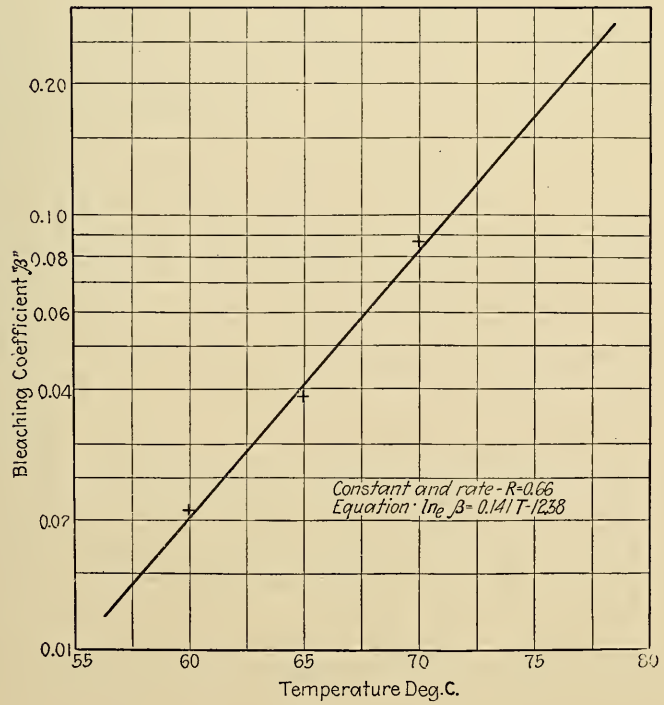


FIG. 3

The slope of each line on Figs. 1 and 2 equal the bleaching coefficient, $-\beta$, for that specific temperature and air rate, as seen from the equation above.

The variation of β with temperature at constant air rate, Fig. 3, is represented by an exponential function as predicted, since the vapor pressure vs. temperature relation in general is exponential. An inspection of Fig. 3 shows that the log of β, when plotted against temperature, gives a straight line, and that the rate of bleaching doubles every 5 deg. C. The equation showing the value of β with variation in temperatures is $\log_e \beta = 0.141\ T - 12.38$.

The rate of bleaching is nearly proportional to the amount of air used, Fig. 4, the line failing to pass through zero due to incomplete

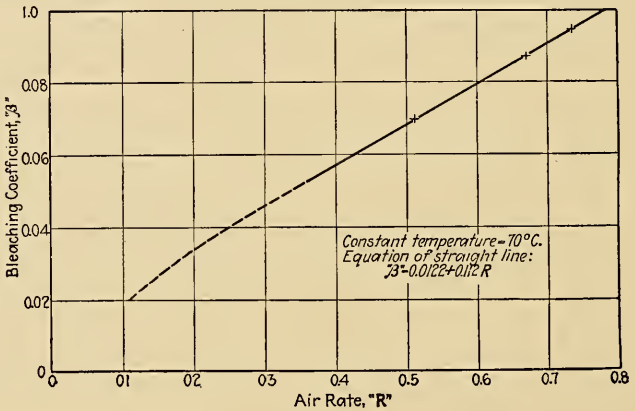


FIG. 4

saturation of the air at the velocities in question. The equation showing the variation of β with air rate is $\beta = 0.0122 + 0.112\ R$. Fig. 5, showing the combined effect of temperature and air rate on the rate of bleaching, is self-explanatory.

Fig. 6 shows vapor pressures of nitric acid and lower oxides above 93 per cent nitric where the lower oxide concentration is 1 per cent. The values calculated by extrapolating data [1] by means of the Clapeyron equation and those experimentally determined points are compared with data by Pascal [2] and Creighton and Githens.[3] The lower

[1] Thorpe, vol. 3, p. 692.

[2] Paul Pascal, *Ann. Chim.*, vol. 15, pp. 253–90 (1921).

[3] H. J. M. Creighton and J. H. Githens, *J. Frank. Inst.*, vol. 179, pp. 161–9 (1915).

oxide vapor pressures are admittedly low, due to incomplete saturation of the air, as already noted. This plot shows the lower oxide pressure

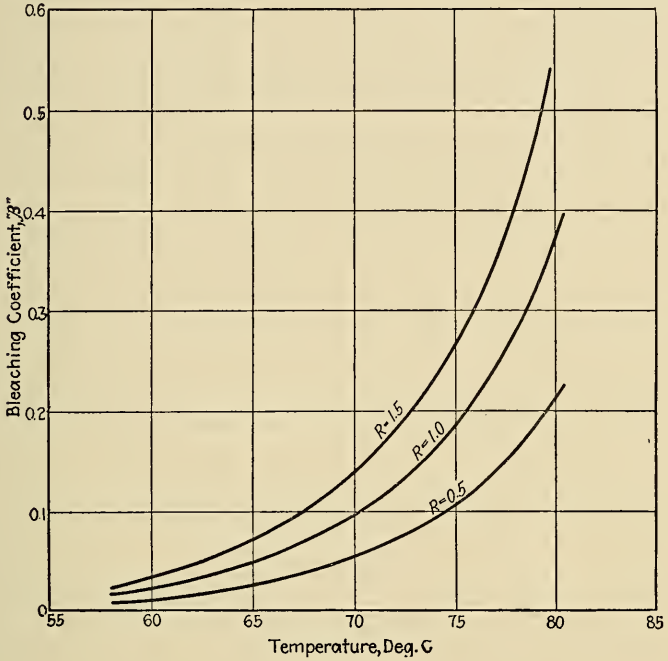


FIG. 5

for a 1 per cent solution, and Henry's law may be used to calculate the pressure above a solution of any other concentration.

These results indicate the advantages to be gained by using a high temperature. An inspection of the integrated equation,

$$\log_e \frac{N_1}{N_2} = \beta(\theta_2 - \theta_1),$$

shows that bleaching between any two concentration N_1 and N_2 requires a time inversely proportional to β, the bleaching coefficient. Since β doubles with a 5 deg. C. rise in temperature, bleaching time at 40 deg. C. therefore would be sixty-four times as long as at 70 deg. C. The effect of air rate may be simplified to the statement that bleaching time is inversely proportional to the air rate employed.

In plant bleaching the temperature of the acid drops during the process due to evaporation of lower oxides and nitric acid. This fact

must be allowed for in applying the constants obtained from laboratory runs. For example, a laboratory bleaching from 0.26 to 0.06 per cent at 70 deg. C. and 0.66 R would require 18 minutes, while a

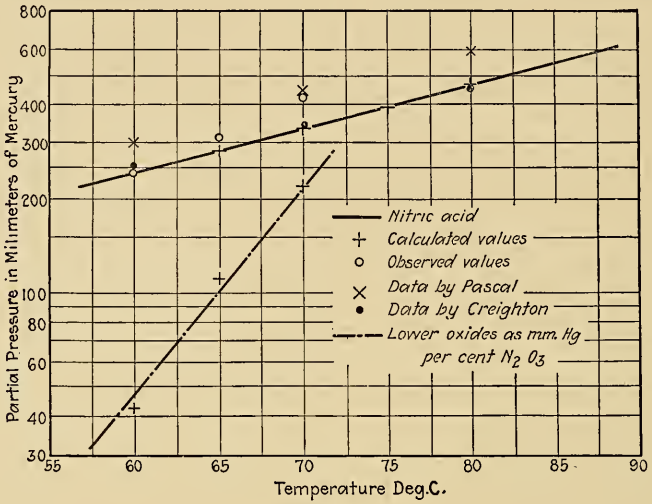


FIG. 6

plant bleach with the same air rate, starting at the same temperature, but finishing at 64 deg. C., would take 32 minutes. For accurate calculation of a plant run, it is necessary to obtain temperatures during the bleaching period, look up the corresponding values of β, plot these against the time, and get an average β from the area under the curve. The application of this method gave checks on the lower oxide removal of better than 10 per cent in all cases. The value of β to be used for this plant run was found at 66 deg. C.—i.e., two-thirds of the difference between 70 and 64 deg. C. subtracted from the higher temperature. This latter rule gives a fairly close approximation in all cases, so that it is unnecessary to use the accurate method mentioned above. Thus, in bleaching an acid high in lower oxides dropping from 70 to 55 deg. C., the average value of β would be 60 deg. C.

Bleaching may be effected by merely heating the acid, providing the vapors have opportunity to escape from the system. It is possible to raise the acid to such a temperature that the lower oxides boil off, the boiling point rising as the oxide content decreases. Some work has been done along this line with the object of determining the opti-

mum combination of heating and air blowing to give the desired bleaching, having in mind the loss of nitric acid, the heat requirements, and the time necessary. The results of this work will be published at a later date.

The loss of nitric acid incurred in bleaching has been calculated from the vapor pressure data shown by the line on Fig. 6. While the results are not strictly quantitative, it can be stated that, in bleaching to a fixed concentration, less nitric acid is lost at the higher temperatures. This statement is corroborated by Fig. 6, where the lower oxide vapor pressure increases with temperature much more rapidly than the nitric acid pressure.

Summary

(1) From theoretical considerations, the equation for the rate of bleaching of nitric acid by air is shown to be

$$\log_e \frac{N_2}{N_1} = -\beta(\theta_2 - \theta_1).$$

(2) Three runs at constant air rate, but varying temperatures, and three runs at constant temperature, but varying air rates, proved this law.

(3) The rate of bleaching was found to be proportional to the rate of air flow and to double with each 5 deg. C. rise in temperature.

(4) The coefficients obtained in the above laboratory runs give calculated rates of bleaching which check observed rates in the plant with an accuracy of better than 10 per cent.

(5) The approximate vapor pressures of the lower oxides of nitrogen in nitric acid solution were determined for a 1 per cent solution.

(6) In bleaching nitric acid to a fixed concentration of lower oxides less nitric acid is lost at the higher temperatures, since the vapor pressure of the lower nitrogen oxides increases more rapidly with an increase in temperature than does the vapor pressure of HNO_3.

THE PRODUCTION OF HYDROCHLORIC ACID BY THE DIRECT UNION OF HYDROGEN AND CHLORINE

By HUGH K. MOORE

Read and discussed at the Niagara Falls meeting, June 19–22, 1922

Fellow Members of the American Institute of Chemical Engineers:

Your Secretary, at the request of the Council, has asked me to complete the symposium on the Manufacture of Acids, by writing an article on "The Production of Hydrochloric Acid by the Direct Union of Hydrogen and Chlorine."

The process as we are using it is a simple one, and I should hardly have thought of making this the subject of a paper had I not been asked to do so. I am impelled to do this for two reasons: first, that I find there is a nation-wide misconception as to the extent to which this process is covered by patent rights; and, second, because of the economic changes which have reversed the process of making chlorine from hydrochloric acid, viz., making hydrochloric acid from chlorine.

In order to clarify the situation, I find it necessary to prepare a chronology which attempts to summarize theoretical developments, patents and industrial events that have had a bearing upon processes for the production of hydrochloric acid by the direct union of hydrogen and chlorine. The chronological treatment has the advantage of showing the growth of theory and practice from year to year. To this end many advantages have been sacrificed that would have been gained by classifying the same material in other ways.

The dates given are usually the dates of publication of the information. In some cases this rule has been departed from. The chronology, however, gives a point of departure for careful work in case questions of priority are ever raised.

Although many sources have been consulted, two of them require special acknowledgment. Marcus B. May, Esq., has lent a valuable file of material dealing with the Roberts patent. Volume II of Mellor's "Treatise of Organic and Theoretical Chemistry" contains a comprehensive treatment of academic research upon the hydrogen-

chlorine reaction. The main dates in the development of the electrolytic-cell industry have been collected from many sources, no one of which deserves special mention here.

It will be noticed that in this chronology there are many conflicting statements by different investigators and the author has made no attempt to reconcile these or to omit those which he believes not to be true. He has simply recorded in this place the pertinent statements of alleged facts as contained in the literature.

1772

Priestley first collected gaseous hydrochloric acid over mercury.

1774

Scheele prepared chlorine from manganese dioxide and hydrochloric acid.

1785

Berthollet concluded that chlorine is an oxygen compound.

1789

Lavoisier concluded that hydrochloric acid contained oxygen.

1801

Cruickshank (*Nicholson's Journ.*, (1), 5, 202, 1801) observed union of hydrogen and chlorine under influence of light.

1807

Sir Humphrey Davy first employed an electric current to decompose a fused salt and in this way separated and discovered the metals, potassium and sodium.

1808

Gay Lussac formulated the law that chemical reactions between gases take place in simple volume ratio.

1809

John Dalton ("A New System of Chemical Philosophy," Manchester, 2, 189, 1811), experimenting with a mixture of hydrogen and chlorine collected over water, observed that a diminution did not take place immediately on exposure to the light, but only after a minute or two; that the more powerful the light, the more rapid is the combination; that the combination is checked by shading the eudiometer, and that bright sunlight causes an explosion.

Gay Lussac and Thenard (*Mem. d'Arcueil,* 2, 340, 1809) failed to deoxidize chlorine and demonstrated that when equal volumes of hydrogen and chlorine are mixed together and exposed to sunlight, they unite with violent explosion, but without change of volume, to give gaseous hydrochloric acid.

1810

Davy demonstrated the elementary nature of chlorine.

1833

Michael Faraday discovered and formulated the laws that govern the action of an electric current in æqueous salt solutions, and determined the electro-chemical equivalents of various processes.

1843–1845

J. W. Draper (*Phil. Mag.,* (3), 23, 401; (3), 25, 1; (3), 27, 327) investigated the reaction between electrolytic chlorine and hydrogen and the part played by light in the reaction. With an instrument that he called a tithonometer, he discovered that—

(1) When light from an electric spark falls on a mixture of equal volumes of hydrogen and chlorine, a sudden expansion occurs and the mixture then returns to its original volume.
(2) A large amount of radiant matter is absorbed before chemical combination takes place; combination then begins slowly and increases in rapidity until a constant rate is attained.
(3) The maximum sensitiveness to light was attained when the gases were present in exactly equal volumes, a small excess of either gas retarding the rate of combination considerably.
(4) "Insolated" chlorine (i.e., moist chlorine that has been exposed to the sunlight), mixed with hydrogen in the dark, combines immediately when the mixture is exposed to diffused daylight.
(5) There is a relationship between the rate of formation of hydrogen chloride (after the "Draper" effect) and the quantity of incident rays.

Draper believed that the first action of light was to produce a more active modification of chlorine.

1851

The patent of Charles Watt (British 13,755 of 1851) covered the preparation of chlorine, soda, hypochlorite and chlorate by electrolysis

of alkali chloride solutions. Kershaw (*Chem. Trade J.*, April 10, 1920) says:

"Watt's patent . . . is a remarkable document of great historical interest, but at that date the dynamo had not been perfected, and as there was no practical means of obtaining large currents for electrochemical work, the electrolytic chlorine manufacture described by Watt remained dormant for another thirty-five years." Watt did not foresee many of the technical difficulties, but he did describe the troublesome secondary chemical reactions.

1854

Charles Watt (British patent 893 of 1854) invented a double-stage bleaching process following a preliminary immersion in alkali. The first bleaching bath consisted of sodium hypochlorite, while the second contained sodium hypochlorite, to which hydrochloric acid was added to release hypochlorous acid.

1857

Bunsen and Roscoe (*Phil. Trans.*, 1857, 147, 355, 381, 601) proved conclusively by quantitative experiments the existence of the period of photochemical induction. They found that the action of light upon a mixture of hydrogen and chlorine is at first very slow, a definite length of time being required in order for it to reach its maximum activity. These authors found, for example, that when a mixture of these gases was exposed to the light of a small petroleum lamp burning at a fixed rate, the amount of hydrochloric acid formed in each minute increased during the first nine minutes, and then became constant. They showed that the presence of oxygen as an impurity retards both the period of induction and the rate of combination. Their observation that an excess of hydrogen lowers the sensitiveness of an electrolytic mixture of hydrogen and chlorine is regarded as an erroneous result caused by the contamination of the hydrogen with oxygen.

They modified the tithonometer of Draper and Sir Henry Roscoe renamed it the actinometer. They used pure electrolytic chlorine and hydrogen.

1865

Henry St. Claire Deville (*Ann. Chim. Pharm., 135* (1865), 94) was able by means of his "hot-cold" tube to show a trace of dissociation of hydrochloric acid at 1,300°.

1868

Deacon and Hurter established the Deacon process for the manufacture of chlorine. British patent 1403 of 1868.

1878

Roscoe and Schorlemmer ("Treatise on Chemistry," vol. I, page 118, N. Y.) described the production of hydrochloric acid by burning hydrogen in chlorine or by the reverse operation. The gases were not produced by electrolytic means.

1879

Becquerel (*Wurtz Dict.*, 1879, 2, 255) suggested that hypochlorous acid is an intermediate compound formed before the hydrochloric acid.

Morgan (British Patent 5030 of 1879), as agent for two Russians, Wastchuk and Glouchoff, received provisional protection for a process and apparatus designed to prevent polarization in electrolytic cells for the manufacture of caustic soda by removing the gases as fast as formed from the two sides of a divided electrolytic cell. They suggested the broad ideas of using the gases in a gaseous galvanic battery and of using the hydrogen to produce heat. According to their later patent, British patent 4985 of 1880, the apparatus described failed to work.

1880

Morgan (British Patent 4985 of 1880) disclosed for his clients (see above) the electrolysis of sodium chloride in a diaphragm cell, and the separate collection of hydrogen and chlorine evolved, which gases are subsequently combined through the agency of a gas battery to form hydrochloric acid.

Paper No. 37, File Wrapper, Roberts, U. S. Patent 807,640.

Paper No. 2, Appeal Card, Roberts, U. S. Patent 807,640.

Wastchuk et al. seem to have had in mind the recovery of energy, and the manufacture of hydrochloric acid was incidental to this. This hydrogen-chlorine cell is an idea that has never become practical, for according to Nobis (Dissertation, Dresden, 1909) hydrogen gas must be passed very rapidly through the cell, less than one per cent being utilized.

See also Allmand, "Applied Electrochemistry" (1920), 219.

1881

Arendt ("Technik der Experimentalchemie," Leipzig, 1881, vol. 2, page 105) published a description and diagram of a process and apparatus for the direct synthesis of hydrochloric acid. The method was a laboratory one only, for the hydrogen was made by use of zinc and hydrochloric acid in a Kipp's apparatus and the chlorine was made by the interaction of hydrochloric acid and manganese dioxide and controlled by a Kipp's apparatus. Here was disclosed a burner consisting of concentric glass tubes, the smaller protruding upwards beyond the larger. The smaller or inner tube conducted hydrogen, while the annulus between the tubes conducted chlorine. The orifices were enclosed in a glass receptacle designed for conducting away the hydrochloric acid formed. Roberts claimed later that this provided for the burning of one gas in an atmosphere of the other, and that unequal amounts of chlorine and hydrogen would be used, which would result in contamination of the product in case of excess chlorine, and waste of raw gases in any case. He successfully evaded this reference by providing for the use of equal quantities of electrolytic hydrogen and electrolytic chlorine and by designing apparatus which caused the two gases to impinge directly upon each other. See Paper 27 of Roberts file wrapper.

Barlow (British Patent 1897 of 1881) collected the oxygen and hydrogen, evolved from water by electrolysis, in separate gasometers and then effected "the synthesis of a compound by uniting two streams of its constituents by flaming combustion." Inasmuch as the oxyhydrogen blowpipe was invented by Robert Hare in 1801 following the invention of the pneumatic trough by Priestley, his invention seems to have been the use of three old steps in a new combination to accomplish an old result.

1882

Nolf (English Patent 4349 of 1882) described a mercury cathode.

1883

Mallard and Le Chatelier (*Annales des Mines,* 1883, section IV, part D) exploded numerous mixtures of hydrogen and chlorine in closed vessels. Upon the pressures there developed they based certain conclusions concerning the dissociation of hydrochloric acid at high temperatures. Haber ("Thermodynamics of Gas Reactions," 110) feels that these observations afford no certain knowledge of the dissociation.

1884

Breur (D. R. P. 30222 of 1884) invented a rigid porous diaphragm made by mixing cement, common salt, and hydrochloric acid.

Berthelot (*Compt. rend.*, 99, 7) reported that equal volumes of chlorine and hydrogen unite without volume contraction at 150° or at ordinary temperature under the influence of the electric spark, when in contact with platinum black or carbon.

Richardson and Grey (British Patent 4417 of 1884) protected the use of electrolytic chlorine for production of bleaching powder. This use was, however, subordinate to the main one of producing caustic and soda to compete with Le Blanc process. This is the first reference available that discloses the use of electrolytic chlorine to form a commercial product.

1885

Victor Meyer and Langer ("Pyro-chem. Untersuchungen," Braunschweig, 1885, p. 67) showed qualitatively that hydrochloric acid dissociates to some extent at 1,700°. Haber calculated that for every 100 volumes of unchanged hydrochloric acid there is 0.2 volume of chlorine and an equal amount of hydrogen. The results of Victor Meyer and Langer are considerably in excess of this, but they used platinum vessels through which hydrogen diffuses at this temperature. See Haber, p. 110.

H. Y. Castner, an American, invented method by making aluminum by reducing aluminum chloride by means of metallic sodium, the sodium being made by reducing caustic soda at low temperature with iron carbide.

1886

Hermite (Eng. Patent 3957 of 1886) also used a mercury cathode.

E. Matthes and Weber (D. R. P. 34888) invented the first commercial cell for caustic soda, known as the Griesheim cell, and employing the solid diaphragm principle.

Rohrman (German Patent 39659) disclosed a method of making nitric acid by causing nitric oxide and air to impinge upon each other to form nitrogen peroxide, which is passed through dust chambers and absorbing apparatus in a manner described. The examiner in the Roberts cases cited this patent repeatedly as an apparatus providing for direct impingement upon each other of two gases capable of chemical union. The contention of the attorney for Roberts was that

this was only one step and that "the invention residing in a process is not carried out . . . until all the steps from the bringing together of the jets of the two gases to the final steps of recovering the product of combination are completed."

Castner established a small experimental aluminum works near Waterloo bridge in London, which was the predecessor of the British Aluminum Company of Oldbury.

1887

Pringsheim (*Wied. Ann.*, 32, 384) suggested that the intermediate compound is chlorine monoxide. He proved that the action of light is less marked with dry gases than with moist gases.

Hall introduced the thermal electrolytic process for aluminium, which ultimately survived all others in the United States. Heroult, the Frenchman, secured independent patent rights on the continent and in Great Britain. See C. M. Hall, U. S. Patents 400,766 and 400,664, April 2, 1889, applied for July 9, 1886, and Paul Heroult, French Patents 175,711, April 23, 1886, and 170,003, April 15, 1887. These obliged Castner to turn his attention elsewhere.

1888

E. A. Le Sueur "commenced work towards a commercial solution of the wet electrolysis of common salt in 1888." See "Note on Certain Unpublished Work on Electrolysis Using Supported Mercury Cathode," *Trans. Am. Inst. Chem. Eng.*, 6, 168.

Brevoort and Isaiah L. Roberts, of Brooklyn, assignors to the Roberts-Brevoort Electric Company of New York, patented a diaphragm of cloth or felt, impregnated with starch jelly. See U. S. Patent 394,638. Meager references have been found to other applications filed at about the same time employing albuminous material, mineral gelatinous matter, and saponified material rendered insoluble. Rogers mentions a Roberts diaphragm compounded of anthracite coal.

1889

Ferdinand Hurter, of the United Alkali Company, published a paper in the *Journal of Society of Chemical Industry*, reviewing previous experience and discouraging continued research on electrolytic cells. The United Alkali Company had, of course, a heavy investment in the Le Blanc process.

Ernest A. Le Sueur developed a commercial electrolyzer for the

production of chlorine and soda products at a chemical works at Newton Upper Falls, Mass.

Le Sueur commenced work on diaphragm type of cell.

1890

Hautefeuille and Margottet (*Compt. rend.*, 109, 641–643), as preliminary to an investigation of the decomposition of water by means of heat in the presence of chlorine and carbon monoxide, investigated the partition of hydrogen between oxygen and chlorine.

Ernest A. Le Sueur graduated from Massachusetts Institute of Technology, his thesis being "Investigation of the Method of Decomposition in a Certain Class of Electrolytic Cells."

The original Griesheim works started with 200 hp.

1890–1891

Le Sueur installed a small demonstration plant at Bellows Falls, Vermont.

1891

The Le Sueur cell was invented.

Castner patented an electrolytic process for manufacturing sodium and potassium.

Hermite and Dubosc (Eng. Patent 21959 of 1891) also used the mercury diaphragm, as did also Greenwood (Eng. Patent 5999 of 1891).

Le Sueur (U. S. Patent 583,330, issued May 25, 1897; British Patent 15050 of 1891) added hydrochloric acid to the anode compartment of his cell, in order to neutralize the caustic soda, diffusing through the diaphragm from the cathode compartment.

Kellner (British Patent 22437 of 1891), of the Kellner-Partington Paper Pulp Company, protected the use of chlorine gas passed counter current to a pulp stream. He claimed the recovery of the hydrochloric acid evolved. From the viewpoint of the hydrochloric acid, the oxidizable material in the pulp would further the reaction. This process has never proved feasible either to bleach pulp or to prepare hydrochloric acid.

1892

The Hargreaves-Bird cell for sodium carbonate (Eng. Pat. 18871 of 1892; 5197 and 18173 of 1893) employed an unsubmerged cathode compartment filled with carbon dioxide. The diaphragm was said to be non-porous to the electrolyte.

The earliest commercial mercury cell was that of H. Y. Castner (1892). English Pats. 16046 (1892); 10584 (1893).

Roubertie, Lapeyre and Grenier (British Patent 15,113 of 1892; German Patent 67,754, August 26, 1892) applied for a patent, which was not granted, for a process in which hydrogen was conducted from the cathode chamber and distributed through the anode liquid. The resulting gases were drawn to a chamber, where union was completed under the influence of light from an electric arc in the anode chamber and in the final mixing chamber. Provision was made for introducing hydrogen from other sources than the cathode chamber and for heating it if desirable. This reference made it necessary for Roberts to withdraw his original general claims, which provided for passing a stream of hydrogen and chlorine into a mixing chamber and leading off hydrochloric acid. Roberts first limited his general claims by specifying that his gases were conducted to the mixing chamber in separate streams.

Ground was broken at Rumford Falls, Me.

Le Sueur started the diaphragm cell and process at Rumford Falls under the financial control of the American Electrochemical Company. Kershaw, *Chem. Trade Journal,* April 24, 1920.

The Griesheim works was doubled in capacity.

1892–1893

Castner was experimenting upon the use of mercury cathode in cell to produce caustic soda.

1893

Freyer and Meyer (*Zeit. phys. chem.,* 11, 28) observed that a mixture of hydrogen and chlorine is ignited if heated in a closed vessel between 170° and 240°, or if the stream of the gas be heated between 430° and 440°. The ignition temperature varies so much with the conditions under which the gases are heated that very variable numbers have been reported. (Mellor) This looks like an anticipation of the Roberts disclosure.

Hemptinne (*Zeit. phys. chem.,* 12, 244, 1893) found a mixture of hydrogen and chlorine at the moment of explosion to be electrically conducting. Trantz and Hengling later cast some doubt on this conclusion.

Vautin (Eng. Pat. 13568 of 1893 and 9878 of 1894; U. S. Patent 541,465, June 25, 1895), of London, Eng., employed a cathode of

molten lead or tin and used fluorides to fuse salts at a lower temperature.

Richardson (British Patent 19688 of 1893) used a Bunsen burner or induction coil in electrolytic chambers as a safety exploding device to prevent the accumulation of dangerous volumes of hydrogen and chlorine, which sometimes occurs accidentally. This reference was cited by the examiner of the Roberts application, when the applicant disclaimed the use of diffused light to initiate the reaction and attempted to claim "the flaming combustion" of hydrogen and chlorine. This reference forced the applicant to qualify his invention further.

First manufacturing began at Rumford Falls.

Outhenin-Chalandre, the Frenchman, invented the cell bearing his name.

1894

H. B. Baker (*Trans. Chem. Soc.*, 1894, *65*, 611) proved that when the mixture of hydrogen and chlorine is very highly dried the combination in daylight proceeds exceedingly slowly, so that 25 per cent of the gas remains uncombined after exposure to diffused daylight for two days and bright sunlight for an equal time.

H. B. Dixon (*Phil. Trans.*, 184A, 97) found that the explosion wave travels at the rate of 1,745 meters per second in the electrolytic mixture of hydrogen and chlorine dried by conc. sulphuric acid, and nearly 1½ per cent slower, or 1,729 meters per second, in the moist gas. With an excess of hydrogen the rate is faster, being 1,849 meters per second in the mixture $2H_2 + Cl_2$, and 1,855 meters per second in the mixture $3H_2 + Cl_2$.

Lorenz (British Patent 25073 of 1894) proposed making hydrochloric acid from free chlorine obtained electrolytically or otherwise by passing the chlorine simultaneously with steam through earthenware retorts, charged with coke, charcoal, anthracite, or the like, and heated to a dark red heat. The reaction $2Cl + H_2O + C = 2HCl + CO$ is stated to take place easily and quantitatively; the CO can be employed for heating the retorts. Nauman (*Zeit. angew. chemie*, 197, 1897) contradicted this statement.

The Bitterfeld plant in Germany started with 2,000 hp.

C. B. Barton started work for the old Electrochemical Company of Rumford Falls, Me., and in 1896 became superintendent of the plant.

Castner patented process for manufacturing caustic soda and caustic potash using mercury layer.

1895

G. and G. W. Bell, of Liverpool (Eng. Patent 20542 of 1895), employed a horizontal porous diaphragm supporting a layer of mercury between the lower anode chamber and the upper cathode chamber. (*J. Soc. Chem. Ind.,* Dec. 31, 1896.) In 1896 they (Eng. 11,133 of 1896) found it necessary to have a roof over the anode chamber with grooves for collecting the chlorine. (*J. Soc. Chem. Ind.,* July 31, 1897.) Finding it necessary to have the mercury flow in and out of a decomposing chamber, they attempted to secure this result by valves changing the head of liquor on the mercury and by intermittent flow (English Patents 25890 of 1897 and 11570 of 1898; *J. Soc. Chem. Ind.,* 18 (1899), pp. 50 and 685). According to Vorce (*Trans. Am. Inst. Chem. Eng.,* 13 (I), 47), the failure of this research led Gibbs to propose the use of a cylindrical electrolytic cell. This was evidently a United Alkali Company project and tends to explain the line adopted by its subsidiaries, the Pennsylvania Salt Company and the Canadian Salt Company.

On June 25, 1895, Isaiah H. Roberts filed application for the manufacture of hydrochloric acid from hydrogen and chlorine. This was issued in 1905. See Freyer and Meyer under 1893.

The Bitterfeld works doubled its capacity.

Castner cells were first operated in America during the latter part of 1895 and January, 1896. Mauran (*Trans. Am. Inst. Chem. Eng.,* 13 (I), 8) states that he built at this time a graphitizing furnace for electrodes after plans of H. Y. Castner.

1896

Chalandre (British Patent 15834 of 1896) added a continuous stream of hydrochloric acid to the anode compartment to prevent secondary reactions.

Huber (U. S. Patent 558,176, April 14, 1896) patented a process involving the use of electrolytic cells to produce hydrogen and oxygen, which are stored in separate gasometers and burned in a specially designed blowpipe for heating purposes. The examiner of the Roberts application cited this as an example of "the synthesis of a compound by uniting two streams of its constituents by flaming combustion." This reference with Barlow (1881) forced the applicant to abandon the words "a flaming combustion."

Mond (*J. Soc. Chem. Ind.,* Oct. 31, 1896) noted that only two

electrolytic works producing chlorine on a really large scale were in operation, both being in the neighborhood of Stassfurt. These were evidently the original Griesheim works and the Bitterfeld works.

A Castner works was started at Ostermienburg, Germany, utilizing 1,500 hp. for the manufacture of caustic potash and bleaching powder. This was in connection with the Deutsche Solvay Company. Later the Solvay modification of cell was adopted.

1897

Lunge and Marmier (*Zeit. angew. chemie,* 10, 105 (1897)) studied the partition of hydrogen between oxygen and chlorine and found 577° C. to be the equilibrium temperature.

Gautier and Helier (*Compt. rend.,* 124, 1128, 1267) kept hydrogen and chlorine mixed between 15 and 16 months in darkness without sign of combination. They found that in light the rate of the reaction was augmented by increasing the proportion of chlorine beyond that required for the reaction: $H_2 + Cl_2 = 2HCl$; similarly also with hydrogen, but the effects were less pronounced than with chlorine. In agreement with M. Berthelot's suggestion, the results were presumably disturbed by the walls of the containing vessel.

The Allen-Moore cell was invented, employing the unsubmerged cathode for producing caustic soda. This feature has revolutionized cells over the entire world so that in all modern cells the cathode is not submerged in the electrolyte. Acheson graphite was first used in the cells.

According to Mauran, the Carborundum Company graphitized electrodes for the Castner people, employing a modified carborundum furnace.

Castner-Kellner Company established works at Weston Point near Runcorn.

1898

Dolezalek (*Zeit. phys. chem.,* 26, 334 (1898)) studied the hydrogen-chlorine cell, the products of which are power and hydrochloric acid. By an indirect method he obtained a mean value of 22,428 cal. for the heat of the reaction. By calorimetric methods Berthelot and Thomsen had found 22,000 calories. See Haber, page 109.

Acker (English Patents 6636 and 6637 of 1898) designed a cell on the same principle as the Vautin cell.

James Mercer put a cell into practical operation at Haverhill,

Mass., which, according to F. G. Wheeler (*Chem. Met. Eng.*, 21, 436), was developed from the Hargreaves cell and was the predecessor of the Gibbs, Wheeler, and Merry-and-Noble cells. Mercer had been a foreman at Rumford Falls.

The Castner Electrolytic Alkali Company's works, using the Castner mercury cell, was established at Niagara Falls in 1898, utilizing 2,000 horsepower. Its successor is the Mathieson Alkali Company. In another place Kershaw specifies 6,000 horsepower and Castner-Kellner cells.

The S. D. Warren Company of Westbrook started an installation of Carmichael cells.

In October, 1898, the plant of the Electrochemical Company at Rumford Falls was transferred to the works of the Burgess Sulphite Fiber Company at Berlin, N. H.

1899

The Acker Process Company built works at Niagara Falls in 1899, employing the Acker fusion process, with molten lead as cathode material in place of mercury. The Acker works was burned down after a few years' operation and has not been rebuilt.

H. and W. Pataky (Eng. Patent 1831 of 1900; French Patent 296,740 of 1900; D. R. P. 114,219 of 1899) passed molecular proportions of chlorine and hydrogen into a vessel charged with coarsely powdered charcoal and set upon a water bath. At the commencement of the operation the apparatus is heated, but subsequently cold water may have to be used in the bath. The charcoal absorbs the gases, which combine without explosion, and hydrochloric acid is set free when the charcoal becomes saturated. Neumann (*Zeit. angew. chemie,* Dec. 13, 1921) says that this process is subject to explosions, caused by local overheating and slight changes in gas pressure.

Works were started at Ponblieres St. Marcel, in France, by the Societe la Volta, which employed the Outhenin-Chalandre cell.

Acheson graphite came on the market.

1900

Chalandre, Colas, and Gerard (U. S. Patent 647,217) described apparatus for collecting the hydrogen and the chlorine from the respective chambers of the cell, burning them, and returning the hydrochloric acid produced to the anode chamber to prevent the for-

mation of secondary compounds, such as hypochlorites and chlorates, by the reaction of chlorine with the diffused sodium hydroxide. This reference is more recent than the Roberts patent. The process was protected by U. S. Patent 665,953, dated Jan. 15, 1901. The process was protected in France by Patent No. 286,923; issued to Societe dite La Volta, March 17, 1899.

1901

J. J. Thomson (*Proc. Camb. Phil. Soc.,* 11, 90, 1901) found that the rate of combination of an insolated mixture of hydrogen and chlorine was not affected by exposure to X-rays, thorium emanations, etc.

1902

J. W. Mellor (*Trans. Chem. Soc.,* 1902, 81, 1292) proved that hypochlorous acid and chlorine monoxide are not intermediate compounds, inasmuch as their introduction does not shorten the period of induction.

Mellor and Russel (*Journ. Chem. Soc.,* 81, 1272) found that if the gases (hydrogen and chlorine) are well dried no explosion occurs in sunlight, and about 30 per cent combined after three days' exposure to June's sunshine. They found no explosion occurred with bulbs of the dried gases at 450°, whereas the moist gases exploded at 260°. Dammer refers to work in 1896 on the same topic. (Storch, *Zeit. phys. chemie,* 19, 1.)

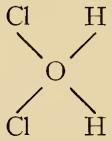
Pauling (British Patent 81828 of 1902) dissociated water at high temperatures, removing the hydrogen from the mixture by adding chlorine.

Masson (French Patent 324,859, Sept. 30, 1902) heated a mixture of chlorine, sulphur dioxide, and superheated steam in a confined space, passing the product through a sulphuric acid tower, and recovering hydrochloric acid.

McDonald (U. S. Patent 697,157, April 8, 1902) invented a three-compartment cell, providing for no difference in hydrostatic head between anode and cathode compartments. McDonald had been a foreman at Rumford Falls. His cells were installed in the plant of the Warner Chemical Company at Carteret, N. J. Experience with this cell resulted in the development of the Nelson cell. This cell is also said to be in use by the D. M. Bare Paper Company of Roaring Springs, Pa.

1903

Bevan (*Phil. Trans.*, 1903, A, 202, 71) showed that the temperature coefficient of the velocity of this photochemical change is smaller than is usually found for purely thermal reactions. He also suggested the intermediate compound:



Heibling (French Patent 330,807, April 4, 1903; English Patent 15212 of 1903) used a reversible silver chloride electrode in an electrolytic cell to produce hydrochloric acid in an intermittent manner.

Askenasy and Mugdan (U. S. Patent 804,515, Nov. 14, 1904) passed chlorine gas through a tower counter current to a stream of sulfurous acid, tapping off concentrated sulphuric acid at the bottom and hydrochloric-acid gas being evolved at the top. This was claimed to be an improvement over a Deacon process (British Patent 3098 of 1898), which produced a mixture of sulphuric acid and hydrochloric acid. The equivalent British Patent is 14342 of 1903 and German Patents 157043 and 157044 are issued to the Consortium für elektrochemische Industrie. This is also the French Masson patent of 1902.

1904

Burgess and Chapman (*Proc. Chem. Soc.*, 1904, 20, 52, 164) showed that a mixture of hydrogen and chlorine which had passed through the period of induction is rendered inactive again by mixing with hypochlorous acid, chlorine water, hydrochloric acid, water, nitrogen peroxide, or chlorine peroxide.

Mellor (*Proc. Chem. Soc.*, 1904, 20, 53) investigated the influence of temperature on the period of induction. He showed that between 3° and 50°, the higher the temperature the shorter the period, while over 38° side reactions apparently took place hiding the effect due to temperature alone.

First Gibbs's cell started, presumably at Wyandotte, Michigan. See Vorce, *Trans. Amer. Inst. Chem. Eng.*, 13 (I), 48.

The Townsend cell developed by Townsend, Sperry, Baekeland, Marsh, etc. (Eng. Pat. 18403 of 1904), employed kerosene in the cathode chamber.

1905

After his application had been ten years in the Patent Office, Isaiah L. Roberts, of Brooklyn, N. Y., secured U. S. Patent 807,640, which was assigned to the Roberts Chemical Company. In the appeal to the Examiners-in-Chief, the attorney for the applicant represented that the Roberts Chemical Company was annually producing 2,400,000 lb. of pure hydrochloric acid, valued at $120,000, an amount equivalent to one-half of all the acid of that grade made in the United States.

The Roberts patent covered a process consisting of the following essential steps:

Claim 1.

1. Producing hydrogen and chlorine.
2. Conducting the two gases in separate streams to a common point.
3. Causing the streams to impinge directly upon each other at such point.
4. Burning the two gases at the point of impingement, one supporting the other without the presence of any other gas.
5. Conducting off and recovering the resulting hydrochloric acid.

Claim 2 differed from 1 in the following particulars:

1. *Continuously* producing hydrogen and chlorine *in the relative proportions in which they combine to form said acid.*

Claim 3 differed from 1 in the following particulars:

1. *Continuously* producing *by electrolysis regulated amounts of* hydrogen and chlorine *in the relative proportions in which they combine to form said acid.*

The British patent for the same process (No. 24733 of 1905) covered one claim, worded essentially as Claim 1 of the American patent. The equivalent French patent is No. 360,829 of 1905; the German patent is No. 194,947 of 1905.

Jorissen and Ringer (*Chem. Weekblad*, 2, 41, 1905; *Ber.*, 38, 899, 1905: 39, 2093, 1906; *Arch. Neerl.*, (2), 12, 157, 1907) found a slight formation of hydrogen chloride after exposing for 33 hrs. a mixture of hydrogen and chlorine to those rays from radium which will penetrate thin layers of glass.

Cote and Febvre (French Patents 356,115 of July 12, 1904, and 358,245 of Oct. 3, 1905) prepared chlorine by the electrolysis of hydrochloric acid, using the hydrogen to form more hydrochloric acid with chlorine. The abstracts concerning these patents seem defective.

Gibbs (U. S. Patent 779,998, Jan. 10, 1905), of the Electric Reduction Company, Ltd., of Buckingham, Canada, patented the method of combining hydrogen and chlorine gases by bringing them into contact in suitable proportions in a combustion chamber, the hydrogen being in excess and heated before contact to a temperature of about 300° C. The furnace is of brick and the apparatus as described does not include cooling coils.

Westhausser (U. S. Patent 791,306, May 30, 1905) passed hydrogen and chlorine through solutions of zinc chloride, aluminium chloride, or tin chloride. He claimed the formation of intermediate compounds that broke up to give hydrochloric acid.

Hoppe (French Patent 352,419 of 1905; D. R. P. 166,598 of 1903; British Patent 6759 of 1905; Austrian 26138 of 1906) passed hydrogen and chlorine into solutions of aluminium chloride, zinc chloride, or tin chloride at a temperature of 100° C. and formed hydrochloric acid. This reaction has been studied by Neumann and his pupils (*Zeit. angew. Chem.*, Dec. 13, 1921). He reports a maximum of 70 per cent Cl_2 converted to HCl at 150° C. with 40 per cent $AlCl_3$ solution.

Everette (U. S. Patent 805,009, Nov. 21, 1905), of Tacoma, Washington, claimed to make hydrochloric acid by subjecting a mixture of water, chlorine gas, and compressed air to refrigeration with compressed air and then subjected the intensely cold mixture to incandescent silica. The details and apparatus of this remarkable process were not described.

The Warner Chemical Company of Carteret, N. J., began the production of pure chlorine gas for use in the manufacture of chlorine chemicals other than bleach. They employed McDonald cells and gradually developed the Nelson cell.

Ten Gibbs cells were in operation in May, 1905.

1906

Tredenhagen (*Ann. Physik*, (4), 20, 133) and C. Killing (*J. Gasbelenchtung*, 50, 90) reported that the temperature of the chlorohydrogen flame is a little higher than Bunsen's flame. The hydrogen flame on a Welsbach mantle in chlorine gives a bright green light.

Burgess and Chapman (*Trans. Chem. Soc.*, 1906, 89, 1399) definitely disproved the intermediate-compound theory by showing that mixtures of moist hydrogen and chlorine, in the absence of impurities, exhibit no period of photochemical induction.

Jorisson and Ringer (*Ber.*, 1906, 39, 2093–98) found that the radiation from radium causes hydrogen and chlorine slowly to combine to form hydrochloric acid.

Luther and Goldberg (*Zeit. phys. chem.*, 53, 43, 1906) confirmed the discovery of Bunsen and Roscoe of 1857 that oxygen inhibits the union of hydrogen and chlorine.

Finley (Eng. Patent 1716 of 1906) employed a double diaphragm dividing the anode and cathode compartments, securing high efficiency but low concentration of caustic soda in the cathode liquor.

Isaiah L. Roberts (French Patent 367,835, July 6, 1906; *J. Soc. Chem. Ind.*, 25, 1156) protected an electrolytic diaphragm, comprising a rigid element of porous material covered by a layer of non-porous material, the latter being maintained in position on the rigid element by means of linen cloth.

The Hooker Electrochemical Company of Niagara Falls began the manufacture of bleaching powder employing Townsend cells, developed by C. P. Townsend and Elmer A. Sperry. See Baekeland, *J. Soc. Chem. Ind.*, July 15, 1907, and A. H. Hooker, *Trans. Amer. Inst. Chem. Eng.*, 13 (Part I), 55 ff.

1907

Vogel von Falckenstein (*Zeit. physikal. chem.*, 59, 313, 1907; *Zeit. Elektrochem.*, 41, 1906) studied the partition of hydrogen between oxygen and chlorine. He found that at temperatures above 600° C. hydrogen has a greater affinity for chlorine than it has for oxygen. See discussions in Mellor, Lewis, Rideal, and Taylor, Haber, etc.

Dr. J. Billiter, an Austrian chemist, invented the Billiter-Siemens cell used by the Kaliwerke at Ascherleben, Germany; by Spiro and Soline, sulphite pulp manufacturers at Krummau in Bohemia; reputed to be used by Farbewerke Höchst; and installed in 1910 in the plant erected by the Niagara Alkali Company, the successors to the Roberts Chemical Company.

Gibbs patent issued for cylindrical cell with unsubmerged diaphragm. The cathode had projections entering the diaphragm. U. S. Patent 874,064 issued Dec. 17, 1907.

Baekeland invented electrolytic diaphragm with base of asbestos cloth filled with alkaline mixture of ferric oxide, asbestos, and an hydroxide of iron. U. S. Patent 855,221.

1908

Sirk (*Zeit. phys. chem.*, 611, 545, 1908) studied the reaction of hydrogen and chlorine in darkness. He concluded that the initial reaction velocity is unimolecular at 242.5°. Doubt was later cast upon this conclusion by Melander.

1909

Nobis (Dissertation, Dresden, 1909) studied the hydrogen-chlorine cell. He was able to produce a current, but less than 1 per cent of the hydrogen was utilized. See Allmand, 219.

Isaiah L. Roberts (U. S. Patent 936,039, Oct. 5, 1909; *J. Soc. Chem. Ind.*, 28, 1144) protected a method of making a diaphragm of woody material and then partially carbonizing it.

Levy (French Patent 406,350, Aug. 20, 1909) purified electrolytic chlorine containing traces of hydrogen by passing over copper or platinum, which served as a catalyzer for the formation of HCl, which may be separated by absorption.

Alysworth (U. S. Patent 914,223, Mar. 2, 1909) manufactured hydrochloric acid from waste chlorine by passing it counter current to hydrocarbons, such as naphthalene, the chlorinated by-product being useful as a fireproofing material.

Chapman and M'Mahon (*Trans. Chem. Soc.*, 95, 135, 959, 1717, 1909; 97, 845, 1910) found that oxygen is not as powerful an inhibitor as nitrogen trichloride. Other inhibitors are ozone, chlorine peroxide, and the gases produced by the interaction of moist nitric oxide and chlorine. Nitrous oxide, chlorine monoxide, and nitrogen simply serve as diluents. In the experiments of earlier workers it is probable that the impurities responsible for inhibition were derived from traces of ammonia or nitrogenous matter in the water present.

1910

Hoppe of Leipzig-Möckern (French Patent 418,731 of July 27, 1910; German Patent 231,221 of April 1, 1909) patented a process depending upon the following reactions. This is really a different theoretical explanation of his earlier process.

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl$$
$$Sn(OH)Cl + 2Cl = SnCl_2 + HCl + O$$

See *J. Soc. Chem. Ind.*, Jan. 31, 1911.

Westhauser (British 21,128, Sept. 10, 1910) seems to have protected the equivalent process.

1912

Nagel (*Chem. Ztg.*, 36, 54, 1912) passed steam and chlorine through coke at 1,000° C. to produce hydrochloric acid and chlorine.

1913

Chapman and Underhill (*J. Chem. Soc.*, 103, 496, 1913) studied the influence of the partial pressure of hydrogen upon the union of hydrogen and chlorine in the presence of light. They concluded that "as the partial press. of the hydrogen is increased from zero, the rate of formation of hydrogen chloride per unit volume of the mixture is at first almost proportional to the concentration of the hydrogen, but the ratio of partial pressure of hydrogen to velocity of interaction rises continuously in value as the proportion of hydrogen is increased, and when the pressure of hydrogen has attained a definite value, the rate of formation of hydrogen chloride becomes a maximum, and then, as the proportion of hydrogen is still further increased, the rate of interaction of chlorine and hydrogen falls very slowly."

Bodenstein and Dux (*Zeit. phys. chem.*, 85, 297, 1913) published data from which they concluded that the reaction of hydrogen and chlorine in the presence of light is of the second order and the speed is proportional to the square of the chlorine concentration; while the concentration of the hydrogen is without influence, if not less than one-fourth the volume of the chlorine be present. The hydrogen chloride formed in the reaction has no influence on the speed of the reaction. Oxygen retards the reaction in such a way that the velocity of all stages of the combination is inversely proportional to the oxygen concentration. Chapman and his co-workers have cast some doubt on the conclusion that the reaction is of the second order.

1914

Melander (*Arkiv. Kem. Min. Geol.*, 5, 1, 1914) found the reaction of hydrogen and chlorine in darkness to be bimolecular.

Le Blanc and Vollmer (*Zeit. Elektrochem.*, 20, 494, 1914) found

that 0.03 c.c. of hydrogen chloride was formed during 50 secs. exposure of a mixture of hydrogen and chlorine to the X-rays. It is estimated that a single electron can bring 10^4 molecules into reaction.

Englestadt (U. S. P. 1,121,910, Dec. 22, 1914) patented a process for making hydrochloric acid by burning a mixture of oxygen, hydrogen, and chlorine.

1915

Taylor (*J. Amer. Chem. Soc.*, 37, 24, 1915) found the reaction velocity of hydrogen and chlorine under the influence of radiations to follow the unimolecular law.

Nelson (U. S. Patent 1,149,210, Aug. 10, 1915) invented the cell used by the Warner Chemical Company at Carteret, N. J.; the Warner-Klipstein Chemical Company at South Charleston, W. Va.; and the Hamersley Mfg. Co. of Garfield, N. J.

1917

P. Mathieu (*J. physique*, 7, 166–72 (1917)) reported that, when a mixture of hydrogen and chlorine is exposed to the spark of an induction coil, explosion occurs only when the mixture has between 8.1 and 85.7 per cent of hydrogen; while when exposed to the radiation from the magnesium flame, the limits are 9.8 and 52.5 per cent of hydrogen. The difference is attributed to the good conductivity of hydrogen for heat.

Peter (U. S. Patent 1,229,509; issued June 12, 1917), of Royal Baking Powder Company, reacted water vapor with chlorine in the proportion of 7 to 3 at a temperature above 200°. Charcoal was used as a catalyst.

Garner and Clayton (U. S. Patent 1,220,411; issued Mar. 27, 1917), of Metals Research Company, caused hydrogen and chlorine to unite in a chamber containing charcoal. They employ hydrogen in excess and recommended at least 50 parts of hydrogen to 35 parts of chlorine. They also recommended a temperature above 340° C.

Baumann (German Patent 305,306, July 31, 1917; *J. Soc. Chem. Ind.*, 27, 414; *Ann. Rep.*, 3, 168, addition to German Patent 301,903, to which no reference has been found) added hydrochloric acid gas to the mixture of chlorine and hydrogen in the explosion chamber to prevent overheating and to make the process continuous.

1919

Chapman and Whiston (*J. Chem. Soc.,* 115, 1264, 1919) found that the speed of the reaction between hydrogen and chlorine in the presence of light is proportional to the radiation absorbed per second and inversely proportional to the concentration of the oxygen.

The British Chief Inspector of Alkali, etc., Works reported under "Muriatic Acid Works":

"With a large demand for soda, it may happen that more chlorine is formed than can be absorbed in the manufacture of bleaching powder, potassium chlorate, and products of like nature. The surplus chlorine has been utilized in part to make hydrochloric acid of the highest grade by its chemical union with its equivalent of the hydrogen also evolved in the electrolytic operation. The pure acid came into competition with that produced by those makers specializing in acid of the purest kind, and was one of the factors causing the fall in number of this class of works from 69 in 1918 to 66 in 1919."

1920

Trantz and Hengling (*Zeit. anorg. chem.,* 110, 237, 1920) found no evidence of ionization during the reaction between hydrogen and chlorine.

Kershaw (*Chem. Trade Journal,* April 24, 1920) states:

"The Niagara Alkali Company also manufacture pure hydrochloric acid by the direct combustion of the hydrogen and chlorine produced from the electrolytic cells—a process which was formerly carried on by the Roberts Chemical Company, who operated this works before the Niagara Chemical Company obtained control. For the manufacture of the ordinary commercial acid (guaranteed free from arsenic) they employ stoneware absorption towers for condensation purposes; but for absolutely pure acid (free from arsenic, selenium, compounds of iron, and chlorine) they employ silica as material for the condensation towers."

1922

Townsend (U. S. Patent 1,414,762, May 2, 1922; filed March 1, 1920; assigned to Hooker Electrochemical Company; 3 claims) employs hydrogen confined in a substantially closed system, supplies chlorine at a substantially constant rate, withdraws the resulting hydrochloric acid from the system, and maintains the desired pressure

within the system by the regulated supply of hydrogen thereto. The apparent advantage is hydrogen economy.

In the foregoing chronology I have touched on the principal outstanding features relating to the chemical end. Inasmuch as this process is primarily due to the inventions in the field of electricity, I feel that I must at least mention a few inventions out of the vast number in this field.

1831

Michael Faraday discovered the principle of electromagnetic induction and constructed an elementary alternating current dynamo using permanent magnets.

1841

Charles Wheatstone constructed the first direct current dynamo.

1845

Wheatstone and Cooke patented the use of electromagnets instead of permanent magnets.

1848

Jacob Brett constructed a self-excited machine.

1867

Sir William Siemens announced the invention of the dynamo electric machine by his brother, Werner. This invention was reached independently and almost simultaneously by Wheatstone and S. A. Varley.

1867

Dynamos were produced on a commercial scale in England.

1870

Gramme invented the ring armature dynamo.

1873

The Siemens-Alteneck or multiple coil armature became the basis of the Siemens dynamo developed by the Siemens brothers and with later modifications by Edison, Hoplanson, and others.

1876

Charles F. Brush perfected the Brush electric dynamo and started the Brush Electric Company, the first manufacturers in America.

1878

Charles F. Brush invented the Brush electric arc light.

1879

Edison invented the incandescent electric light.

1880

American Electric Company at New Britain, Conn., began to develop the arc-light system known as the Thomson-Houston system.

1881

Siemens and Halske built a third-rail electric railway in Berlin and an overhead wire line in Charlottenburg.

1882

The Thomson-Houston Electric Company succeeded the American Electric Company. It later became the General Electric Company.

1883

First practical electric railway built in America by consolidation of Field-Edison interests after litigation of three years.

1886

Elihu Thomson announced the invention of electric welding, which was an important factor in reducing the price and increasing the efficiency of the 550-volt dynamo. This dynamo was used at Rumford Falls.

The reaction for the direct union of hydrogen and chlorine is extremely simple, viz., $H_2 + Cl_2 = 2HCl$. It might be interesting to calculate the theoretical temperature of combustion. The heat of formation of 1 gm. molecule in kg. calories is as follows:

H + Cl ordinary temp. 22—Thompsen.
H + Cl ordinary temp. 22—Berthelot.
H + Cl at 2000° C. 26—Berthelot.

Mean sp. ht. $HCl = 0.249 + .0000166\ t$ (Pier Bjernum) Lee Nauman. *Z. angew. Chem.*, 32, I, 141 (1919).

Then $22000 = 36.47\ (.249 + .0000166\ I)\ I$ starting at 0° C.

$$= 9.085\ I + .000606\ I^2$$

$$I = \frac{-9.085 \pm \sqrt{9085^2 + 4 \times 22000 \times .000606}}{.001212}$$

$$= 2120°\ \text{C.}$$

Mol. of ht. $HCl = 6.50 + .0010T$ (Lewis & Randall), *J. Amer. Chem. Soc.*, 34, 1128 (1912)

$$\text{Mean sp. ht. kg.} = 0.178 + .0000274\ \frac{T_2 - T_1}{2}$$

$$= 0.178 + .0000137\ (T_2 - T_1)$$

If $T_1 = 300$, mean sp. ht. $= 0.174 + .0000137\ T_2$

$$22000 = 36.47\ (.174 + .0000137\ T_2)\ (T_2 - 300)$$

$$= 6.35\ T_2 - 1902 + .00050\ T_2 - .15\ T_2^2$$

$$.00050\ T_2^2 + 6.20\ T_2 - 23902 = 0$$

$$T_2 = \frac{-6.20 \pm \sqrt{6.20^2 + 4 \times 23902 \times .000050}}{.0010} = 3090$$

$$270$$

$$t = 2820°\ \text{C.}$$

Mol. sp. ht. $Cl_2 = 6.50 + .004\ T$ (Lewis, Randall)

$$\text{Mean sp. ht. kg.} = .0917 + .0000565\ \frac{T_2 - T_1}{2}$$

$$= .0917 + .0000282\ (T_2 - T_1)$$

If $T_1 = 300$, mean sp. ht. $= .0832 + .0000282\ T_2$

Mol sp. ht. $H_2 = 6.50 + .0009\ T$

Mean per kg. $= 3.23 + .00045\ T_2 - T_1 = 3.23 + .000225\ (T_2 - T_1)$

If $T_1 = 300$, mean per kg. $= 3.162 + 2.000225\ T_2$

$$26000 = (T_2 - 300)\ [35.46\ (.0832 + .000282\ T_2) + 1.008\ (3.162 + .000225\ T_2)]$$

$$= (T_2 - 300)\ (2.955 + .0010\ T_2 + 3.187 + .000227\ T_2 = (T_2 - 300)\ (6.142 + .00123\ T_2)$$

$$= 6.142\ T_2 + .00123\ T_2^2 - 1840$$

$$.00123\ T_2^2 + 6.142\ T_2 - 1840 = 26000$$

$$.00123\ T_2^2 + 6.142\ T_2 - 27840 = 0$$

$$T_2 = \frac{-5.773 \pm \sqrt{5.773^2 + 4 \times 27840 \times .00123}}{.00246} = 2970$$

$$270$$

$$t = 2700^\circ \text{ C.}$$

(As this is only calculated with slide-rule accuracy, 270 is used instead of 273.)

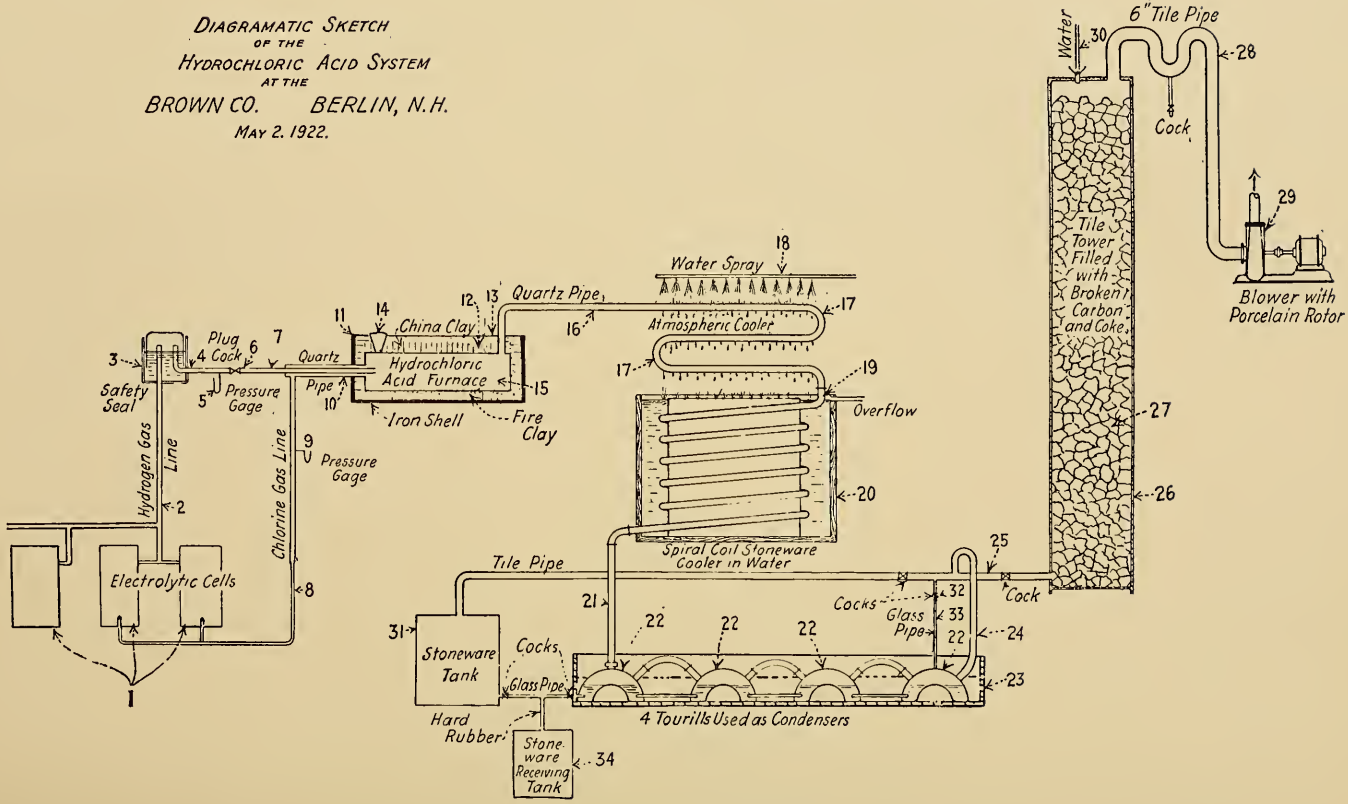
From the above it will be seen that the temperatures of combustion must necessarily be very high in any process in which pure chlorine is united with pure hydrogen. The chemical engineer in all probability would never attempt to carry on such a process commercially after he had made the above calculations unless there was some special reason for requiring pure hydrochloric acid gas. He would at once foresee the difficulties which would result from expansion and contraction of the materials used and he might have misgivings as to the effect of these gases at such high temperatures on the materials used. Hydrochloric-acid gas, fortunately, need not be pure to obtain a high-grade muriatic acid. He would naturally add hydrogen enough to combine with all the chlorine and probably an excess. If he uses air as a diluent for the sake of reducing the temperature, he would also add more hydrogen in order that it should not be deflected beyond the necessary amount by its combustion with the oxygen in the air and thereby give a muriatic acid containing free chlorine.

The relative amounts of hydrogen and chlorine are easily obtained for these gases in every installation (without exception, I believe) are obtained from the electrolysis of a solution of either sodium chloride (or potassium chloride), and the end products for such electrolyses are two molecules of either sodium hydrate (or potassium hydrate), one molecule of hydrogen, and one molecule of chlorine.

$$2NaCl + 2H_2O = 2NaOH + H_2 + Cl_2$$

The regulation of the relative amounts is accomplished by the relation of the number of cells whose cathode compartments, producing hydrogen, are connected together, to the number of cells whose anode compartments, producing chlorine, are connected together. Inasmuch as these cells are usually connected in series, it will readily be seen that the relative amounts of hydrogen and chlorine do not alter with the alterations of current going through the cells.

DIAGRAMATIC SKETCH
OF THE
HYDROCHLORIC ACID SYSTEM
AT THE
BROWN CO. BERLIN, N.H.
MAY 2. 1922.



The capacity is dependent on the number of cells connected on the anode side into this circuit, the amperes per cell, the efficiency of the cells, bearing in mind that there must always be at least enough hydrogen to unite with all the chlorine. The capacity will vary with the current passing through the cells.

From the foregoing chronology it will be seen that the industrial manufacture of caustic soda, chlorine, and hydrogen was a direct result of the invention of the direct current dynamo whereby the large amount of mechanical energy in our waterfalls could be transformed into electric power at a low cost. As long as electro decomposition was dependent on the current produced by batteries, there could be no progress, as the cost was prohibitive. With the dynamo in commercial use an impetus was given to the perfection of cells for the electrolytic decomposition of salt brine. With the improvements in the last-mentioned process the production of chlorine and hydrogen was so cheapened that it was found possible to produce the hydrochloric acid needed in an electrolytic plant cheaper than the acid could be bought delivered at the works. The large amount of water contained in muriatic acid, being approximately three and one-half times the weight of the dry gas, made freight rates for the acid itself high. The necessity of shipping in glass carboys and the freight on these both ways, also the breakage and interest on the large amount of investments in these containers, also militated against shipping this product any considerable distance. The union of hydrogen and chlorine also produces a chemically pure hydrochloric acid, and this fact alone stimulated the production along these lines.

Having now briefly touched on the underlying economic factors leading to the production of hydrochloric acid from chlorine instead of the production of chlorine from hydrochloric acid, let me briefly describe by a diagrammatic sketch how we produce hydrochloric acid at the Brown Company at Berlin, New Hampshire.

Referring to the diagram, (1) are electrolytic cells producing both hydrogen and chlorine. The hydrogen from these cells passes through a pipe (2) to a safety seal (3) and from thence through a pipe (4) to the quartz pipe (7). In pipe (4) there is a water-pressure gauge (5) and a cock (6). The chlorine, which leaves the cells (1) only from a less number of cells than the hydrogen leaves from, enters tile pipe (8) containing a water-pressure gauge (9), entering a quartz T pipe (10) surrounding quartz hydrogen pipe (7) entering

the furnace (11). This furnace consists of an iron shell (11) lined inside with fire-brick (12). The brick is laid up in china clay. The tops of the bricks are also covered with china clay. The quartz tubes (7) and (10) need not be flush with each other where they enter the furnace, as this is unimportant. Near the end of the furnace is a small opening stopped ordinarily by an earthenware plug (14). It is in this furnace that the combustion takes place, which will be later on explained. The gases emerge from the combustion chamber (15) through a quartz pipe (16), which, by means of S bends (17), form an atmospheric cooler, cooled by a water spray from pipe (18). The S bends (17) are connected with an earthenware spiral coil (19) immersed in water held in tank (20). Coil (19) is connected by pipe (21) to a set of tourills (22) immersed in water held in tank (23), and the gases not absorbed by them enter pipe (24), and then pipe (25) to the bottom of tower (26), filled with broken carbon and coke (27). The top of this tower is connected by pipe (28) to an exhauster (29) with a porcelain rotor. Water enters the tower through pipe (30). The water entering the tower, after running through the coke, runs out of pipe (25) to a stoneware tank (31). This acid, about 17 per cent, is usually strong enough for our purposes. If, however, stronger acid is needed, we open cock (32) in pipe (33), allowing a certain amount of acid to pass through the cooled tourills (22). This acid may be collected in tank (34). This is, in brief, the description of the apparatus for making hydrochloric acid from the direct union of hydrogen and chlorine.

Having now explained the diagram, I will proceed to describe the process of manufacture. First, the exhauster is started, thereby creating a slight vacuum on the whole system. The water is then turned onto the cooling apparatus, plug (14) is removed, and a piece of waste impregnated with oil is inserted. This is then lighted, after which the hydrogen is turned on by opening cock (6). When the furnace is good and hot the plug (14) is inserted and the chlorine is drawn in. The water is turned into the absorption system and the process is running. The safety seal (3) is made of very light tin and blows off when there is an explosion, thereby relieving the pressure on the entire system, so that it is not demolished should there be an explosion.

Inasmuch as the furnace may have to stand wide variations of temperature according to the purity of the gas, it is necessary that

the inlet and outlet pipes be made of a material which must not only withstand the action of the acid at these high temperatures, but take care of these wide temperature ranges. After much experience we have found nothing to take the place of fused quartz. Its extremely low coefficient of expansion renders it invaluable for this purpose. It is this low coefficient of expansion which allows us to spray it while white hot with water and yet not crack it. Fused quartz will not, however, stand a temperature of over 1,200° C., nor will it stand that long, so it is absolutely necessary that the temperature of combustion be reduced far below the theoretical. Inasmuch as a vacuum is always maintained on the chlorine side of the cells, the necessary amount of air will suck in with the chlorine if too much care is not taken with that part of the cell to make it tight. We keep about an inch of water pressure on the hydrogen part of the cells.

Of course, the temperatures actually obtained at different parts of the process will depend upon such variables as concentration of the Cl_2 used, quantity of Cl_2, excess of H_2, air leaks, cooling water used, etc.

In order to give you an approximate idea of at least the minimum range of temperatures, I obtained one day recently the following data. Owing to lack of production, the cells were run at a very low amperage, so that the amount of hydrogen and chlorine produced was extremely small, while the air leakage was necessarily an increased percentage of the total.

Per cent Cl_2 in gas entering furnace	4.0
Per cent H_2 in gas leaving furnace	0
Temperature of H_2 entering furnace	63° F.
Temperature of Cl_2 entering furnace	55° F.
Temperature in furnace	1470° F.
Temperature of gases entering atmospheric cooler	680° F.
Temperature of gases leaving atmospheric cooler	370° F.
Temperature of gases leaving submerged cooler	130° F.
Theoretical production of HCl for day, pounds	121

The essential factors involved in the most successful operation of this system are:

(1) Continuous operation.
(2) Maintaining of H_2 supply under a small pressure to exclude possibility of air leaks.

(3) Use of strong Cl_2 gas with a large excess of H_2 to keep down operating temperatures.
(4) Extreme care in the starting of the system.
(5) Plenty of cooling water.

There are different methods of starting up the furnace, but probably as good a one as any is as follows:

(1) Start blower at end of system.

(2) Insert piece of waste, well soaked in kerosene oil, through the small hole at top of furnace. Ignite and start H_2 into furnace. When it gets burning well insert earthenware plug and cover over with china clay.

(3) In a few minutes allow the Cl_2 to be drawn into the furnace.

If carried out in this manner, a good start is obtained, and the possibility of blowing up the whole apparatus is reduced to a minimum.

From the above it will be seen that the process is extremely simple both as to construction and maintenance.

The process requires absolutely no labor in that it runs itself as long as the cells are running. This plant will thus run weeks without anybody paying any attention to it, with the product turned out regularly. It is, in effect, the only manufacturing plant which I have ever seen of which I can heartily approve. We can have no labor troubles here, for there is no labor.

In conclusion, I want to acknowledge my indebtedness to Mr. Gordon L. Cave for his help in preparing this chronology.

Discussion

President Howard: That is a very interesting paper, but you have not told us what the process is.

Mr. Richter: Hydrogen and chlorine are united by taking the gases from the cathode and anode compartments of a number of cells. In that way our proportions are maintained. The temperature within the combustion chamber is very high, and I think we have measured at times as high as 1,600. The temperature drops rapidly in the air-cooled compartment, which consists of quartz, and averages 400° F. as it enters the quartz coil. It leaves 100° to 200° F. and passes through the absorption tower and then to the tourills if we

wish to make a stronger acid. The tower is filled with coke. We may absorb with other surface material for a better acid, but for our particular purposes we are not much interested in that now. It may be interesting to know the method by which we start the operation. We spent some time experimenting with the spark plug idea of setting off a spark and so on. But we got away from that very soon, and at the present time it is done by a little burning waste. The operation is continuous and sometimes for three weeks no one goes near the combustion chamber, and very little trouble has been experienced in the maintenance. The chamber is about 3 feet inside by 12-inch cross-section and production, so far as we know, seems almost unlimited. We have never reached a place where we failed to get the combination of the two elements.

PRESIDENT HOWARD: Is there any explosion in connection with it?

MR. RICHTER: We have had in the early stages two or three, but I don't remember any one within the last three or four years.

PRESIDENT HOWARD: Any further question?

PROFESSOR WHITE: I would like to ask what is the normal gas composition entering the furnace?

MR. RICHTER: It is generally from 5 to 30 per cent. Normally it is probably 20 to 30.

PROFESSOR WHITE: And the hydrogen would be——

MR. RICHTER: That is fairly pure, 98 to 100 per cent.

PROFESSOR WHITE: So that it would be 75 or 80 per cent hydrogen and the rest chlorine?

MR. RICHTER: There are considerable quantities of air in the chlorine and therefore the hydrogen percentage is much less than 75 or 80 in the furnace.

MR. HASWELL: Is there any special provision used for protection?

MR. RICHTER: None except the fire-brick which happened to be there. You may be interested to know that the particular operation that we are carrying out is described fairly well in the patent by Englestead, who was with us at that time.

PRESIDENT HOWARD: An American patent?

MR. RICHTER: Yes.

A NEW VESSEL FOR THE ABSORPTION OF HYDROCHLORIC ACID

By STEPHEN L. TYLER

The absorption of hydrochloric acid gas in water at first sight seems to be a very simple proposition. The gas is highly soluble in water and it would seem that simply bringing together the gas and the absorbent would readily result in complete absorption.

The problem, however, is not quite as simple as it would first appear. The solution of hydrochloric acid gas in water is one which is highly exothermic and the solubility of the gas is inversely proportional to the temperature. As an example of this, it is possible at a temperature of 0° C. to dissolve over 500 volumes of the gas in one volume of water, while at a temperature of 60° C. less than 350 volumes of gas can be dissolved in one volume of water, and at a temperature of 110° C. only about 160 volumes may be retained by one volume of water.

The solution of hydrochloric acid gas in water is dependent upon the following conditions:

1. The temperature of the gas and the liquid.
2. The concentration of the gas in the gases to be scrubbed and the concentration of the acid liquid to be produced.
3. The time of contact between the gas and the liquid and the average distance between the gaseous particles and the liquid particles, and also the thickness of the liquid layer and on its motions internal and as a whole.

Three general methods suggest themselves for the bringing about of intimate contact between the gas and the absorbing liquid:

1. Spraying of the liquid into the gas.
2. The bubbling of the gas through the liquid.
3. Contact between the liquid and the gas by a distribution of the liquid over relatively large surfaces.

The first method mentioned above is not practical nor efficient in the case of hydrochloric acid because of the high heat of solution and the difficulty of satisfactorily removing the heat generated. By this

first method only acid of low strength can be obtained. The second method, while reasonably satisfactory from the standpoint of producing acid of good strength when the apparatus is designed for the removal of heat, is impractical from the mechanical standpoint because of the highly corrosive nature of the gas to be handled and the pressures encountered. Thus we have left only the third method or the direct exposure of the liquid to the gas for the satisfactory production of a high strength hydrochloric acid.

At the present time two general methods are used for bringing about this intimate contact between the soluble gas and the absorbing liquid. One of these methods employs stoneware vessels so designed that a relatively large surface of liquid is exposed to the gas. These vessels are also designed for cooling. The second method uses the vertical tower with a suitable packing material over which the absorbing liquid is passed, thus exposing extremely large surfaces of absorbing liquid to the gas. This latter method is used extensively where gas concentrations are low.

The tourille type of plant is very satisfactory for the production of the higher strengths of acid, and the design of the apparatus is such as to allow of very satisfactory cooling and surface exposure of the absorbing liquid to the gases. There is, however, the objection to this plant of its requiring much floor space and necessitating many connections to maintain a circulation of both the liquid and the gas. The tower has been used extensively for the absorption of hydrochloric acid gas, but from this it is only possible to produce acids of low strength, as it is not practical to construct absorption towers with sufficient cooling to keep the tower temperature down to a point where high strength acid may be produced.

A new type of absorption vessel has recently been developed. The general design of this vessel is shown in Fig. 1. It will be seen that the vessel follows the general design of the S bend, but has broadened body (3) which is flattened so as to give large surface with relatively small volume. There is a dam or weir (4) at one end of the lower surface which retains a certain quantity of liquid in the bottom of the vessel, thus making this a small reservoir. By following the S bend principle the pieces would be set up vertically one above the other, the socket (2) receiving the spigot (1) of the vessel following, thus making an absorption system which amounts to practically nothing more than a single conduit through which both the

gases and liquid pass and which has pockets or reservoirs which retain a certain amount of the liquid. This means that the third method of bringing about the intimate contact between the gas and the absorbing liquid is used, but that all of the objections to the other types of apparatus have been removed by the elimination of small tube connections to maintain the circulation of the absorbing liquid. These connections have been made generally of glass, with rubber used as

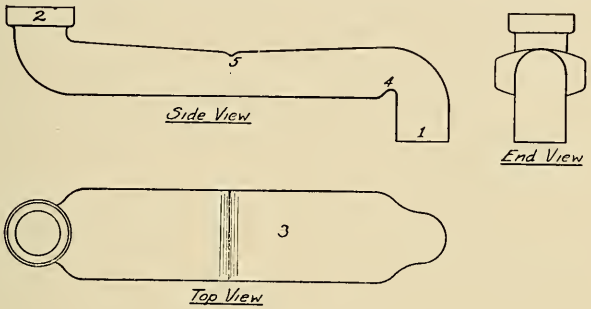


FIG. 1

the packing material, and have been a very objectionable point, especially because of the fact that they were of necessity located below the level of the absorbing liquid and a leak was certain if breakage occurred or the packing deteriorated.

At the central portion of the roof of the vessel there is a low point (5) toward which the vessel slopes from either end. This sloping of the roof will deflect the gases downward upon the absorbing liquid and bring about very intimate contact. There will also be a certain amount of liquid which has condensed out from the gases, and also some of the liquid which has run over from the absorption vessel immediately above which will drip off at this point, making practically a liquid curtain through which all of the gas must pass. This dropping of liquid on to the absorbing surface has the added advantage that it brings about a complete agitation of the absorbent and thus materially increases the absorption. In absorbing soluble gases in liquids agitation of the absorbent will always increase the efficiency. There is also further agitation of the absorbent as it flows from one vessel to the other below, as there is a vertical drop of several inches.

Surface exposure only is more satisfactory for the absorption of gases of higher concentrations, so that the type of vessel just de-

scribed, if used alone, is more especially adapted to gases such as are generated from the pan side of a salt-sulphuric hydrochloric acid plant. In cases where the hydrochloric acid gas concentration is low the same type of absorption vessel may be used, set up in much the same manner, but with interposed packed towers of larger section than the pipe connections themselves.

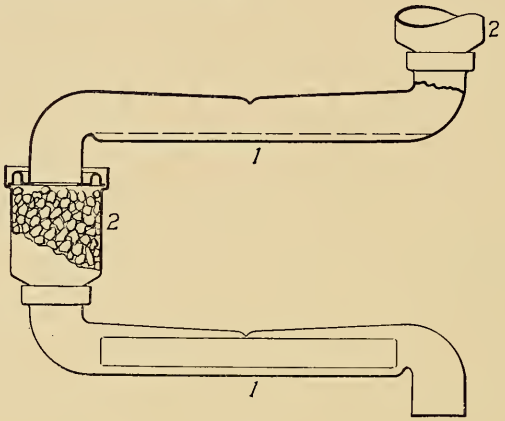


FIG. 2

A set-up showing these short towers is shown in Fig. 2. The packed tower (2) is placed between two absorption vessels (1). The objections already raised to the tower method of absorption in that it did not allow of the removal of the heat generated is overcome in this method of employing towers. The absorbent is thoroughly cooled in its travel through the absorption vessels placed intermediate between the small towers.

Fig. 3 shows a typical cooling and absorption system for hydrochloric acid produced from the gas generated on the pan side of the pan and roaster type of plant. It will be noted that the gas first passes through a water-cooled condenser (1), which will remove much of the condensable vapors and lower the temperature of the gas. The condensate produced in this line runs off from a trap (2). The gas passes on through a second trap (3) and up into the absorption system (4). The absorption system operates on the reflux principle, so that the strongest gas is in contact with the strongest acid. In the upper portion of this, where the gas concentrations are much lower, towers (5) are interposed between the absorption vessels so

as to remove as much as possible of the soluble gas. The gases passing on through this upper portion of the absorption system are carried over to the final scrubbers. The acid produced in the absorption system is taken off from trap (3). The entire absorption system would be thoroughly water-cooled, preventing a rise in temperature due to the absorption and ensuring the production of acid of good strength.

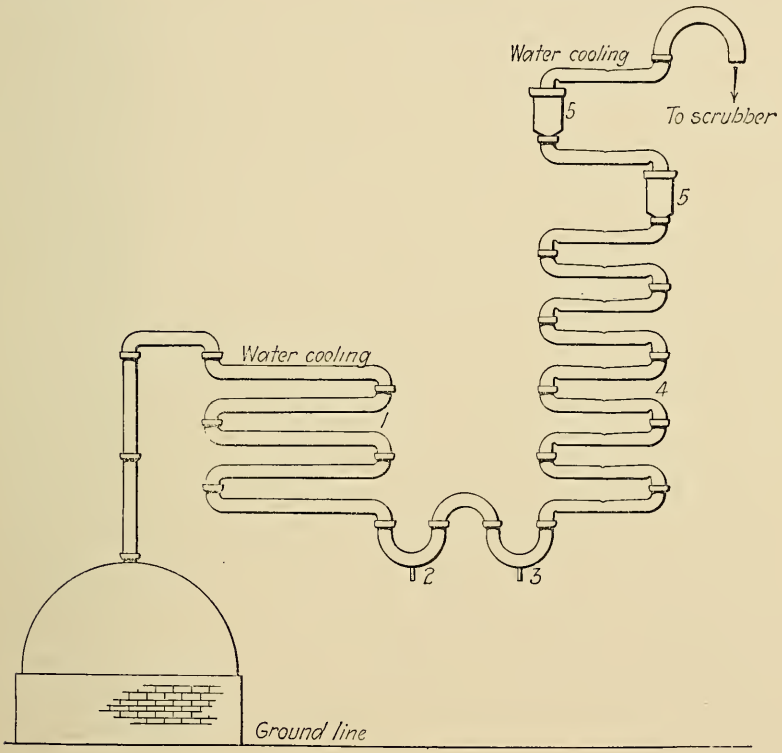


FIG. 3

Fig. 4 shows the general design of a cooling and absorption system for the hydrochloric acid gas produced on the roaster or muffle side of the plant. The gases leaving the muffle are first conducted through a series of S bends (1) which are air-cooled only, then through a second series of S bends which are water-cooled (2). In this latter set of condensers (2) the condensable vapors are removed and the gas is cooled. The condensate from both of these coolers is carried

off through the trap (3). The gases pass forward through another trap piece (4) and up through the absorption system (7), which is composed entirely of absorption vessels (5) with intermediate towers (6). The exit gases from this absorption train are carried over to a scrubbing system, which may consist of another absorption system similar to the one shown, or may be a stoneware tower depending considerably upon the ultimate use for the acid produced.

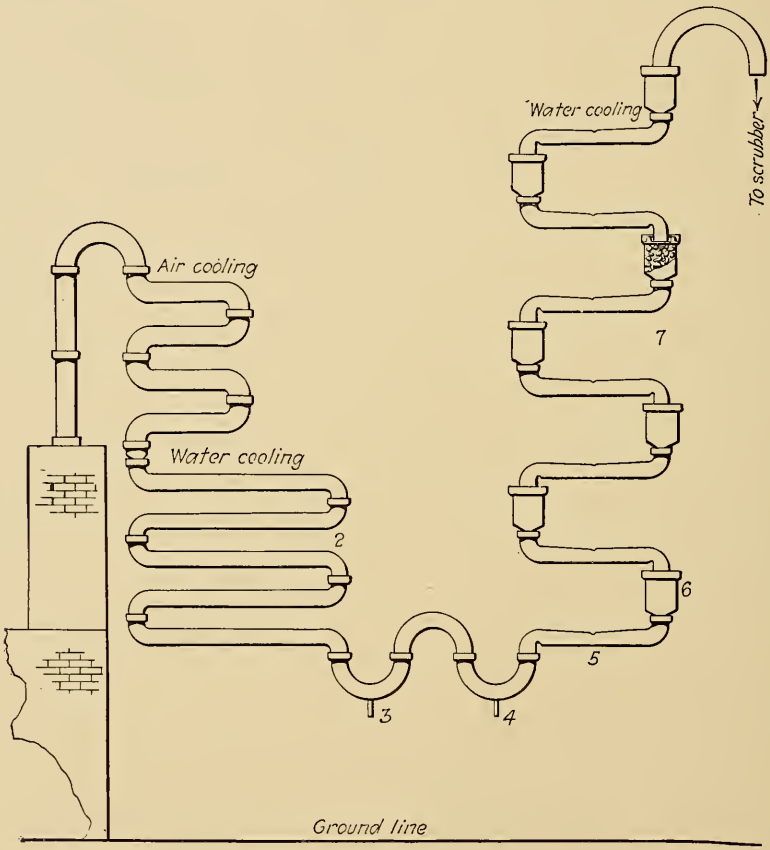


FIG. 4

The type of hydrochloric acid absorption equipment with which this paper deals is designed to be made of fused silica. For such work as this fused silica is especially well adapted, inasmuch as it is insoluble in the acid, and thus the product can not be contaminated.

The wall thickness on pieces made up of fused silica is much less than that obtained in any other ceramic material, thus tending toward increasing the efficiency of the cooling, which, of course, considerably reduces the size of the plant. Fused silica equipment is relatively light in weight, so that the matter of supporting may be readily taken care of with light supports.

In summing up the points brought out regarding the type of absorption equipment described the following points are worth notice:

1. Light weight.
2. Economy of floor space.
3. Complete agitation of absorbent.
4. Liquid curtain through which gas must pass.
5. No joints below liquid level.
6. No glass tube connections or rubber joints.
7. Thorough cooling of gas and liquid.
8. Intermediate towers give all advantages of tower absorption with none of the disadvantages.
9. Complete distribution of cooling water over large cooling surface.

Other uses for the absorption vessel are apparent, but the following are possibly worth mentioning:

1. As absorber for soluble gases other than hydrochloric acid.
2. For bringing about reactions of gases upon solutions, emulsions, or suspensions. An example of this would be some of the chlorination reactions. In this sort of work the use of the intermediate tower should considerably increase the efficiency of the plant.
3. For the concentration of volatile liquids of boiling points approximately that of water.
4. For fractional distillation of liquid mixtures.
5. As condenser for such vapors as nitric acid where surface exposure to the hotter gases is desirable to insure uniformity of product. The large surface exposure as well as the intimate contact between the hotter still gases and the condensate produced when operating on the reflux principle would give an acid of very good quality and color.

Discussion

President Howard: This paper is open for discussion.

Mr. Ermot: Where is the water introduced in that absorption system?

Mr. Tyler: At the highest point on the train. The cooling water may be introduced through special tube entering the absorption vessel through a drilled hole or through a special tube which is fitted into the socket of the vessel—that is, embedded in the packing material.

Mr. Ermot: When you have the two sides as shown in that last diagram, you would have to add water on both sides?

Mr. Tyler: No; the air- and water-cooled condenser would be simply to remove any sulphuric acid which might carry over and also cool the gases.

Mr. Walker: Is it true that there is only one notch in the S bend?

Mr. Tyler: Yes.

Mr. Walker: Why not have more of those notches?

Mr. Tyler: More of these would defeat the purpose of the sloping roof of the vessel and probably eliminate entirely the possibility of forming a liquid curtain through which the gases would pass.

Mr. Leverett: I should like to ask about what area is exposed to the action of the gas?

Mr. Tyler: We have not had an absorption vessel with surface larger than four square feet, but expect shortly to have one of six square feet.

President Howard: Any further discussion? I would like to ask Mr. Tyler what he uses for packing in the sockets.

Mr. Tyler: In the first portion of the plant, where the object is simply that of cooling the gases, the most satisfactory material would be asbestos rope and fiber of sufficient amount to just fill the socket. In the portion of the plant where the absorption takes place a similar packing should be used, but the top surface covered over with an asphaltic cement known as Mastic and produced by the Barber Asphalt Company.

President Howard: Without any binder?

Mr. Tyler: Yes; without any binder. The top can be sealed over with a thin layer of acid-proof cement to seal any openings that there may be.

President Howard: What packing do you use in your tower filling?

MR. TYLER: Coke has been very satisfactory.

PRESIDENT HOWARD: I noticed the little projection at the bottom of those horizontal sections extended over the tops of those tower sections. What prevents the cooling water from dropping off there? Do you have a spray of water running down over those sections?

MR. TYLER: I don't think I get your point.

PRESIDENT HOWARD: You have water cooling?

MR. TYLER: Yes; water cooling on the outside.

PRESIDENT HOWARD: How do you keep the water cooling off the packed joints?

MR. TYLER: It is not necessary to do that.

PRESIDENT HOWARD: You let it go over them?

MR. TYLER: Yes; on the absorption side of the plant the entire system of absorption vessels and towers may be inclosed in a wooden tower with proper ventilation and thoroughly sprayed.

PRESIDENT HOWARD: Have you some of those units in use?

MR. TYLER: Yes.

PRESIDENT HOWARD: I think the system looks like a very interesting one and a very simple one. There is one point, though, that I would like to make a slight correction in—that is, in one of your statements. That is about the tower system not being available for making concentrated acid on account of the inability to cool the water. One of the usual methods in Germany for condensing muriatic acid is to have a series of three or four towers with devices called inter-coolers between them, with a large volume of acid being circulated or recirculated over the towers, and with the acid at the bottom going over the inter-cooling.

MR. TYLER: I had particular reference to the use of large towers for the absorption of hydrochloric acid gas in which the absorbent was not recirculated or cooled and in which no provision was made for the removal of the heat generated. This type of absorption is usually carried on in a single tower of very large size and the acid produced is of low strength because it is necessary to feed an excess of water to prevent overheating.

PRESIDENT HOWARD: Is there any further discussion?

DR. PRATT: I would like to ask Mr. Tyler what size intermediate towers he is using between the S curves.

MR. TYLER: The drawings shown here were drawn up for a six-inch absorption vessel on a six-inch line. The intermediate towers are of 12 inches diameter and about two feet in length.

TANK CARS FOR TRANSPORTATION OF MURIATIC ACID

Read at the Niagara Falls Meeting, June 22, 1922

By J. M. ROWLAND

Chief Engineer, Hooker Electrochemical Company

Tank cars for shipping muriatic acid have in the past been of two general types, viz., single and multiple units. The tanks have been built of wood which has been treated by impregnation or coating with acid-resisting compounds to withstand chemical attack. Experience has shown that the maintenance cost has been high. In order to develop a container that will better resist the chemical action as well as the racking strains of transportation, several different types and materials of construction are now under test. We are concerned here only with the work that has been under the writer's direction, and will endeavor to outline the reasons that led up to the present design and give the results obtained to date.

Development of the Idea

In 1914 the Hooker Electrochemical Company manufactured its first muriatic acid, which was obtained as a by-product from the chlorination of benzol. The plant was enlarged in 1916 to a daily production of approximately 30 tons of muriatic acid. With this production the question of storage became important and wooden tanks were provided for this purpose. The tank staves were impregnated by boiling in tar before assembling, and after assembling several coatings were given. The tanks leaked badly, so a number of different compounds and mastics were tried, but without success. A tank would be tight for a short time and then start a small leak that would gradually increase. Without storage, all acid produced had to be caught directly in carboys, which was far from satisfactory. After spending six months and going to a material expense in an endeavor to make the wooden tanks reliable, we heard of unvulcanized para rubber lining, and immediately installed one storage tank

of 8,500 gallons capacity. This gave good service and later two more were installed.

After the armistice, monochlorbenzol production dropped very low and with it acid production. It was then our company started making its "Hooker White" and "Chemically Pure Hydrochloric Acid" which is made by the direct union of the two gases.

The process for making muriatic acid by burning proper proportions of hydrogen and chlorine, whereby hydrochloric acid gas is formed, has been simplified and developed to such a state that it can be done successfully on a commercial basis. The hydrochloric acid gas as it comes from the burners is of very high purity, so the question of making muriatic acid of high purity resolves itself into preparing pure water for the reaction with the gas, and in using apparatus throughout of such character and quality that it will not contaminate the acid.

These factors have been satisfactorily worked out by the use of distilled water for the absorbing medium and by extreme care being taken in the selection of all materials used for construction purposes, from the burners through the cooling and absorption system, and including the handling, storage, and final shipping containers.

Grades of Muriatic Acid Made

Several kinds of acid are prepared in any density up to 22° Bé. Our commercial muriatic acid is yellow in color from the dissolved iron contained in it and contains also small amounts of lime salt, but absolutely no arsenic or heavy metals. Iron runs less than .005 per cent, non-volatile .005 per cent, and sulphuric acid .0014 per cent.

"Hooker White" muriatic acid is the next higher grade produced, and with the exception of color, which is kept below .0001 per cent iron, is practically the same in composition as the commercial muriatic. The "White" acid fills an important need in such places as the manufacture of dyes and their intermediates, food products, etc. "Hooker C. P. Hydrochloric Acid" is the highest grade produced and runs less than .0001 per cent iron, .0001 per cent non-volatile, and less than .0001 per cent sulphuric acid. These are the only impurities present in this grade of acid; it is used in the manufacture of especially fine products requiring materials of the highest grade.

Acid-Resistant Tank Lining

Such purity, once obtained, must be maintained and it was found that the unvulcanized rubber would accomplish this as well as glass. Therefore, the rubber-lined storage became more important. One of the storage tanks, about two years ago, had the rubber lining of the bottom entirely destroyed by benzol. Through an accident some chlorinated benzol went over with the acid into the storage and settled to the bottom of the tank in a layer probably one or two inches deep. When this was discovered the tank was emptied and the damaged rubber removed. The lining was stripped to a level about 8 inches above the bottom. The acid-soaked wood of the tank bottom was washed and neutralized and a new light wooden flooring laid on top of the old bottom wood. This was given a new rubber lining which was carried up on the tank walls and bonded with the old rubber. This repair was successful, was accomplished quickly, and the tank has been in continuous service ever since without leakage or showing signs of any weakness.

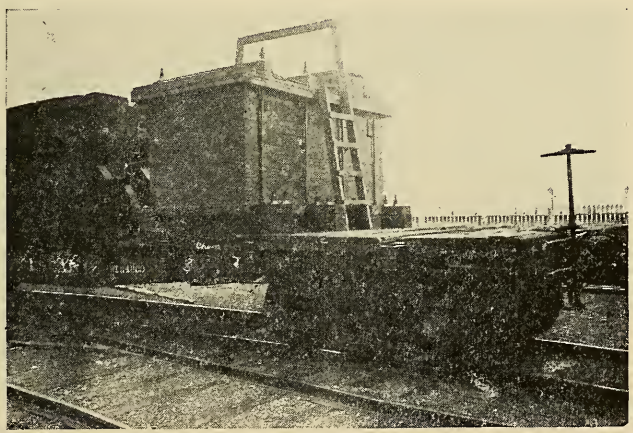


Fig. 1

Fig. 1. Early Stage of Development of the Hooker Tank Car for the Shipment of Muriatic Acid

In 1919 our company was anxious to make tank-car shipments, but, owing to the difficulties that others were having, it did not wish to invest in any of the tank cars that existed at that time. On account of the successful and satisfactory results it had experienced with the

stationary storage tanks made of wood and lined with pure unvulcanized rubber, it decided that this material was worth further study for transportation purposes, and late in the year of 1919 the author was detailed to carry through an investigation. The experience of others who had experimented with transportation tanks lined with para rubber was discouraging, as several attempts had met with failure.

Construction of the Tank Car

As far as could be learned, the experiments had been tried entirely with cylindrical tanks placed in a horizontal position, and the failure had resulted from the rubber lining loosening and dropping away from the top of the tank. This failure was attributed to two principle causes, viz., (1) the racking strains of transportation, which are not met with in quiet storage, and (2) acid being spilled or overflowing the top of the tank, soaking through the wood or the joints between the staves, and destroying the canvas friction which acts as a bonding medium to secure the rubber to the wood.

In view of the above difficulties an experimental tank of rectangular shape was designed in January, 1920, and, after further physical tests of the materials, was constructed and put into service in September. This tank was mounted on one end of a flat car (see Fig. 1) and, with the remainder of the car loaded with carboys, made three trips from Niagara Falls to the Pittsburgh district.

In April of 1921 this tank was mounted on a permanent car, together with three additional tanks of the vertical cylindrical type, and has been in continuous service ever since (see Fig. 2). At the same time a second car fully equipped with vertical cylindrical tanks was built. The service of these two cars proved satisfactory and in September, 1921, the writer was instructed to build nine additional cars, eight for the service of the Hooker Electrochemical Company and one for service in Mexico.

These cars were all built from the same design as illustrated by Fig. 3, each car being equipped with four vertical cylindrical cypress tanks lined with pure unvulcanized para rubber. Each car will carry approximately 35 tons of 21° Beaumé hydrochloric acid.

The work was started September 7, 1921, the first car completed October 15 and the ninth November 2. Owing to the short time allowed, it was necessary to buy existing gondola cars, strip them, overhaul the underframes and trucks while the tank work was pro-

gressing separately. All cars have operated continuously since being put into service with no tank leakage to date. On return to the plant the tanks have been opened, washed, and inspected internally on an average of every second trip. From January 1 to May 15, 1922, the fleet of ten cars has been 996 car days en route and 354 car days at the plant, or approximately 74 per cent of the time away.

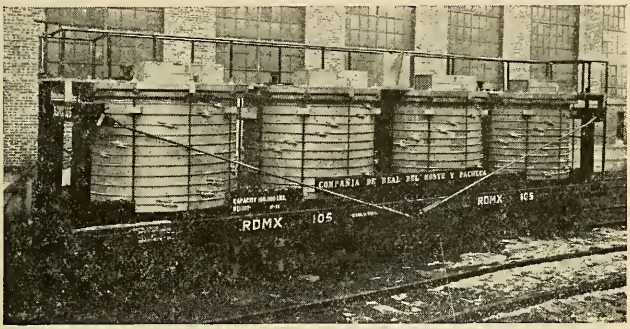


FIG. 2

FIG. 2. Intermediate Stage of the Development of the Hooker Tank Car for the Shipment of Muriatic Acid

Inspection of the 40 tank linings to date shows no failure of the rubber from chemical attack or mechanical strains. Two tanks have had the rubber lining of the bottom punctured by a metal pipe which was used for unloading. These were repaired without removing the tank covers and are in service in good condition. The seven cylindrical tanks installed on the first two cars in April, 1921, showed failure of the cover lining within a few trips, and in the design of the cars built last fall further steps were taken to guard against this weakness.

DETAILS OF CONSTRUCTION

After completion of the last cars the covers of the above seven tanks were removed and rebuilt in accordance with the latest design, and to date there has been no indication of any further cover failure. It is interesting to note that while these covers failed, there was no injury to the tank body. The experimental tank above mentioned, which has now been in service for 20 months, was designed as an open-top tank, with the cover a separate unit, so that failure of the cover would not injure the tank, and to accomplish this the rubber

lining of the inside of the tank was carried over the tank edge and a few inches down the outside; this principle has been followed on all succeeding tanks. The experimental tank is rectangular in shape, being 4 feet wide by 8 feet long by 4 feet high and placed in a transverse position at the end of the car. It is of laminated construction, the sides being built of 2 x 4 cypress laid flat, spiked together, and having dowel bolts at the dovetail corners, and also about 24 inches spacing between. When tanks for a full car were designed the vertical cylindrical shape was adopted for the following reasons: Economy in construction; to keep all metal on the outside of the wood; to keep the joints between staves vertical; and to secure the largest bearing area for the tank load. Experience to date has justified these features.

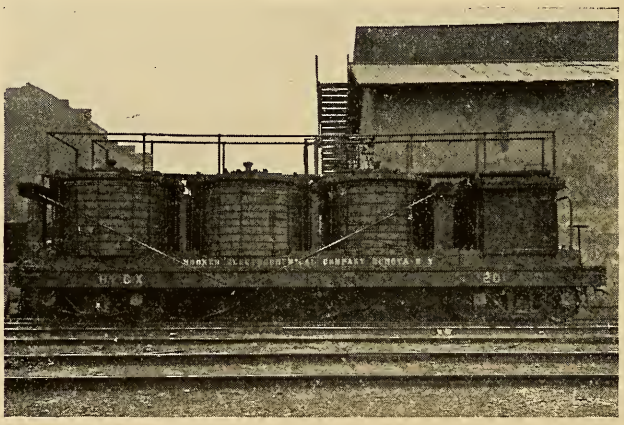


FIG. 3

FIG. 3. Present Stage of Development of the Hooker Tank Car for the Shipment of Muriatic Acid

In constructing the last nine cars all car decking was removed and the tank dunnage carried on heavy wooden stringers that are supported by and secured directly to the steel frame of the car. This renders the steel underframe accessible for inspection, cleaning, and painting, and removes the menace of an acid-soaked deck against the steel. The underframes used are of the fish-belly type. On them are mounted four longitudinal yellow pine stringers. The central stringers are bolted directly to the center sills and transmit through

bearing blocks the individual bottom thrust of each tank to the center sills. The side stringers are also provided with bearing blocks. At each end of the car is a heavy wooden bolster beam near the top of the tank, and by means of struts in the tanks and blocking between the tanks the upper strains are transmitted to the bolsters, and in turn to the side sills near the center of the car through the diagonal tie rods. In addition to the above and to assist against the overturning moment, the covers are provided with holding down bolts that extend down through the main stringers. The most severe test to date of this anchorage was car HECX 205, which was in collision of sufficient force to break the draft gear and the 12 x 14 yellow pine bolster; a careful examination of the tanks, however, failed to show any injury to the lining or balance of the anchorage.

Each tank cover is equipped with a permanent built-in siphon extending into a well in the bottom of the tank; also a vent, measuring well, and manhole. Each car is equipped with a permanent siphon priming apparatus consisting of a water jet vacuum pump, sight bottle, and rubber tubing to reach the furthest siphon. With this device, by connecting a ¾″ water hose to the vacuum pump the siphons may be primed and all four tanks unloaded at the same time without the necessity of opening any tank, without fume, and without introducing water or priming liquid into the acid of the tank, this last being important where acid of high purity is desired. When the car is standing on a level track the tanks can be emptied entirely except for such acid as runs back the 1½″ hose when the siphon breaks from air entering its suction. At the plant these siphons with their priming device are in daily use with good success.

In a recent test a siphon was broken and reprimed 26 times in emptying a tank to determine the time consumed and particularly the difficulties in priming at lower levels. The primes varied from a full tank to ½″ depth in the tank and at no time did it require more than one minute to make the prime.

Acid Resistance of Unvulcanized Rubber

The writer has received the suggestion from one of the rubber manufacturers that possibly HCl in its gaseous state might penetrate the para rubber sufficiently to destroy the friction fabric which is used as a bonding medium between the rubber and the wood. This is of particular interest and it has been observed that the friction fabric

when exposed to HCl fume alone will be destroyed; but whether or not this fume can penetrate the unvulcanized para rubber, and how long it would take, is a question yet to be determined. At the present time physical tests are being conducted which it is hoped will throw some light on this question, and also further tests are under way to determine with what success the para rubber may be cemented directly to the wood without the use of friction fabric. The writer does not anticipate failure of the rubber lining in the tank cars above described due to fume penetration of the rubber because the quiet storage tanks have shown no evidence of this after many years' service, and to date the rubber lining of the transportation tanks shows no sign of racking strains, or evidence that its condition is different from the quiet storage.

Summary

To summarize our company's experience with unvulcanized para rubber lining, we have the following facts: We have had in service of quiet storage one tank five years, one tank four years, one tank three years, and have had no trouble whatever with leakage, and have made one major repair with ease and success when the rubber was ruined by a foreign substance. In the transportation service we have had one tank in continuous operation for 20 months without leakage, and have, at different times of inspection, cut away samples for examination and patched the spots so cut. We have had two cars or seven additional tanks in continuous service for more than one year with no tank leakage. The covers of these seven tanks, however, were renewed. We have had for seven months eight cars or thirty-two tanks in continuous service without leakage or repair of any character except two tanks which were punctured by an iron pipe. We have received favorable reports from one car containing four tanks that went to Mexico, and are advised that it has made five trips to date and has shown no leakage.

In conclusion, the writer believes that muriatic acid tank cars with unvulcanized para rubber lining are a success from the viewpoint of design, cost of operation, and initial cost. Their reliability is a marked advantage. When a car returns it is a help to be able to reload and ship it out immediately and not be obliged to delay several days for repairs. The unvulcanized para rubber is a delicate material and when handled properly will give the desired results. Its success is dependent upon extreme care in design and construction.

Discussion

Vice-President Smith: This very interesting and important paper is before you for discussion.

Mr. Mauran: I would like to ask Mr. Rowland about the cover to the tanks, as to whether there is any other substance than the rubber lining to make the joint tight between the cover and the tank.

Mr. Rowland: No; the rubber lining of the cover is secured to the wood inside the diameter circle of the tank, beyond that it is free, and after the cover is mounted its lining is folded down and joined on the outside to the lining of the tank which projects on the outside of the staves.

Mr. Mauran: And I understand that the lining of the cover and the lining of the tank project outside and are cemented together. Is there any danger of the rubber squeezing out by reason of the pressure?

Mr. Rowland: Some evidence of the enlargement of the rubber is noticeable there from the pressure, but it has never given way.

Mr. Bacon: May I ask what you mean by Para rubber? Does that mean Para rubber from Brazil or from the plantation of Para trees?

Mr. Rowland: I really don't know whether it makes any difference whether it comes from Brazil or not.

Mr. Bacon: The rubber from Brazil is generally superior to plantation rubber.

Mr. Rowland: I think it comes from plantations. The rubber company has taken care of that part in furnishing the right thing.

Mr. Bacon: There are a good many sources of rubber. There are some 400 kinds of trees, but the plantation rubber is very heavy and is recognized as the best grade, although it does not come from Brazil as a rule, and is mostly plantation rubber. A very little of it is grown artificially in Brazil.

Mr. Griswold: I don't know whether it is pertinent to the shipping of muriatic acid, but we have built white pine storage tanks of considerable size which we impregnated with coal-tar oil under pressure of 150 pounds, the staves were scraped and redressed to take out change in the surface that took place in impregnation, and we carefully watched it and saw no leakage at all for quite a number of years.

MR. BACON: I am also wondering whether, if the staves of your tank had been rough instead of dressed, you would not have needed fabric of that kind to secure the bond.

MR. ROWLAND: In order to finish the wood to receive the rubber, we have rubbed and sandpapered and given a coating of cement with a brush. The object is to do away with all sharp edges and rough corners, to provide a smooth surface for the cement to be applied to.

MR. BACON: I believe that the great trouble with the old system of asphalt paving was very largely due to the precautions taken to get a smooth surface to adhere to. I believe that the old style of asphalt paving, which was very apt to break out in sections, would have been all right if instead of applying concrete bottom they had applied it on the loose stone.

MR. ROWLAND: I think the reason is really more to guard against any small particles which might puncture the rubber, and the bond that is secured by the preparation of the wood in this way is sufficient.

TRANSPORTATION OF LIQUID CHLORINE IN FIFTEEN-TON TANK CARS

By J. L. K. SNYDER and H. P. WELLS

Paper read and discussed at the Niagara Falls meeting, June 19–22, 1922

The liquid chlorine industry dates back to 1888, when R. Knietsch of the Badische Anilin und Soda Fabrik discovered that iron and a number of other common metals are not attacked by anhydrous chlorine. He was the first to realize the fundamental fact that, for commercial liquefaction, a chlorine gas had to be used which was of high concentration and free from moisture, and his discoveries pointed the way to the construction of commercial liquefying machinery. Although liquid chlorine was an article of commerce on the continent from that time on, twenty years elapsed before it was produced in the United States on a commercial scale.

The earlier uses for liquid chlorine in this country were for the sterilization of water, the bleaching of textile materials and shellac, the conditioning of flour, the manufacture of laundry solutions and sterilizing and disinfecting solutions, the preparation of drugs and chemicals, and for the separation of metals. The latest—and by far the largest—field is in the bleaching of chemical wood pulp, in which field it is now an established success, and is rapidly supplanting the use of bleaching powder. The interest now manifested in this commodity by paper manufacturers and paper-mill engineers, and the large tonnage requirements of that industry, draw wide attention to the important subject of containers and their transportation.

The following types of containers have been approved by the Bureau of Explosives for use in the transportation of liquid chlorine, namely, cylinders of several sizes up to 150 pounds capacity, ton drums, and fifteen-ton tank cars. The approved types of cylinders are similar in construction to those used for a number of other compressed gases with which you are familiar, and as it is the purpose of this paper to describe the major containers, we will not discuss the specifications for the manufacture of and the regulations for handling cylinders.

Ton Drums

One-ton drums (Fig. 1) have been approved for use in transporting chlorine, sulphur dioxide, and methyl chloride, covered by Shipping Container Specification No. 27, under which ruling the drums must not contain more than 2,000 pounds of liquid chlorine and must have at least 0.8 pounds of water capacity for each pound of permissible liquid chlorine capacity.

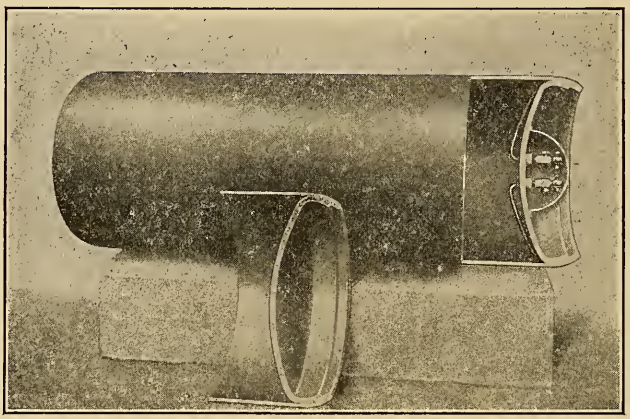


Fig. 1

The drums are made of open-hearth steel with carbon, phosphorus, and sulphur contents falling within definite limits, and with a wall thickness such that at a pressure of 500 pounds per square inch the calculated fiber stress is not in excess of 17,500 pounds per square inch. All joints and seams are made by the forge-lap-weld process and are thoroughly hammered or rolled to insure a perfect weld. The heads are flanged not less than four inches and are dished concave under a red heat to a radius equal to the diameter of the shell. Each drum is finally uniformly and properly annealed and subjected to a hydrostatic pressure of 500 pounds per square inch and an air-pressure test of 250 pounds per square inch.

For filling and emptying the drum, two eduction pipes are provided internally, extending in opposite directions towards the perimeter, and connected to cut-off valves on the head of the drum. When these pipes are in a vertical line, one may be used for the eduction of liquid and the other for gas. The valves are protected

by a steel bonnet 3/16″ thick, which can be quickly and easily removed or put in place.

Each drum is equipped with six safety plugs (Fig. 2), three screwed into each head, filled with fusible metal of fusing point approximately 150 degrees F. These are arranged in such a way that those in one end are equally staggered with those in the other, thus some are in the liquid space and some in the gas space. The purpose of these plugs is to relieve the contents before a pressure is reached sufficient to rupture the drum in case of exposure to fire. Should one of the plugs in the liquid space yield, a stream of liquid chlorine will issue from the drum, therefore it is obvious that the drums should never be placed in hot-water baths to maintain a steady pressure when gas is being withdrawn.

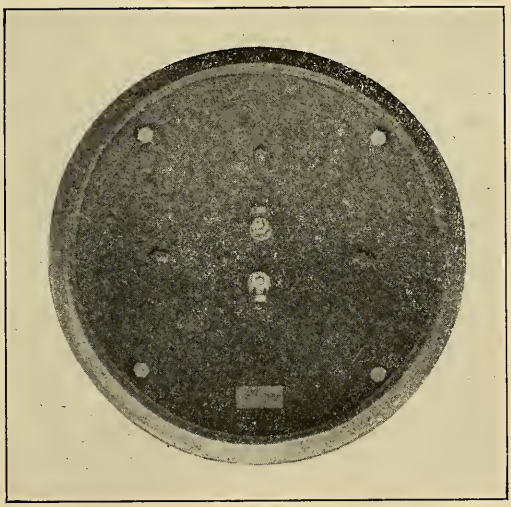
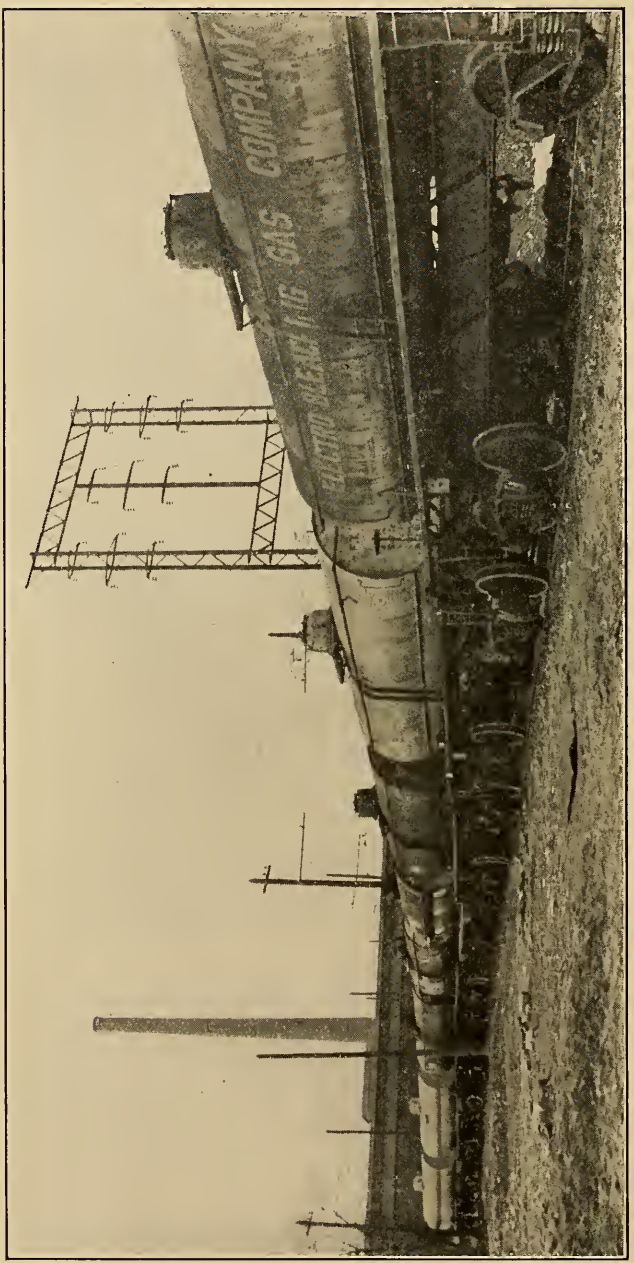


FIG. 2

Ton drums are always shipped in carload lots of twelve or fifteen mounted on cradles anchored to gondola cars or permanently fastened to a specially built steel underframe car with no sides They may be unloaded in place or removed from the car at the consumer's plant. The type of drum in general use measures thirty inches in outside diameter and eighty inches in over-all length, and weighs approximately 1,260 pounds, freight charges being levied on the container as well as on the contents.



PART OF ELECTRO BLEACHING GAS CO.'S FLEET OF TANK CARS READY FOR LOADING

Fifteen-Ton Tank Car

This car carries a single tank holding fifteen tons of liquid chlorine, which has been approved by the Bureau of Explosives for the transportation of chlorine and sulphur dioxide, and is classified by the American Railway Association as Class V tank car. This car is the one type of container now approved by the American Railway Association on which no freight charges are levied, either outgoing or returning, and is therefore of great economic importance to the consuming industries.

This type of car was developed in Germany and was used there for many years prior to the time when liquid chlorine became an article of commerce in the United States, and is, therefore, the oldest major container. Fifteen-ton tank cars were introduced into the United States in 1910 and at the present time there are 42 Class V tank cars in use in this country. Of this number, about 39 are used for the transportation of liquid chlorine, in many cases between points 700 to 800 miles distant, while the remainder are used in the transportation of sulphur dioxide.

The underframe is all steel, and, like the anchorage, draft attachments, wheels, axles, journal boxes, safety appliances, and other appurtenances, is built in accordance with the American Railway Association Standard Specifications for Class V Tank Cars.

Tank.—All plates are of steel complying with the American Society for Testing Materials Specifications for Steel Plates for Forge Welding, the minimum thickness allowed for tanks 60 inches in diameter or under being ¾ inch for the head and shell. The calculated bursting pressure, based on the lowest tensile strength of the plate, must not be less than 960 pounds per square inch. All seams and the connections of the anchorage to the shell are welded by the water-gas process, hammered or rolled, and the seams annealed after welding. No riveting or calking is permitted. Tank heads are dished to a radius of not over five feet, for pressure on the concave side. There is a 15-inch man-hole provided in the top, covered by a steel cover-plate bolted down tight against vapor pressure, a special gasket being used in a tongue and groove joint. The tanks are subjected to a hydrostatic test of 300 pounds per square inch before being placed in service, and are retested every two years in the same manner under regulations of the Bureau of Explosives.

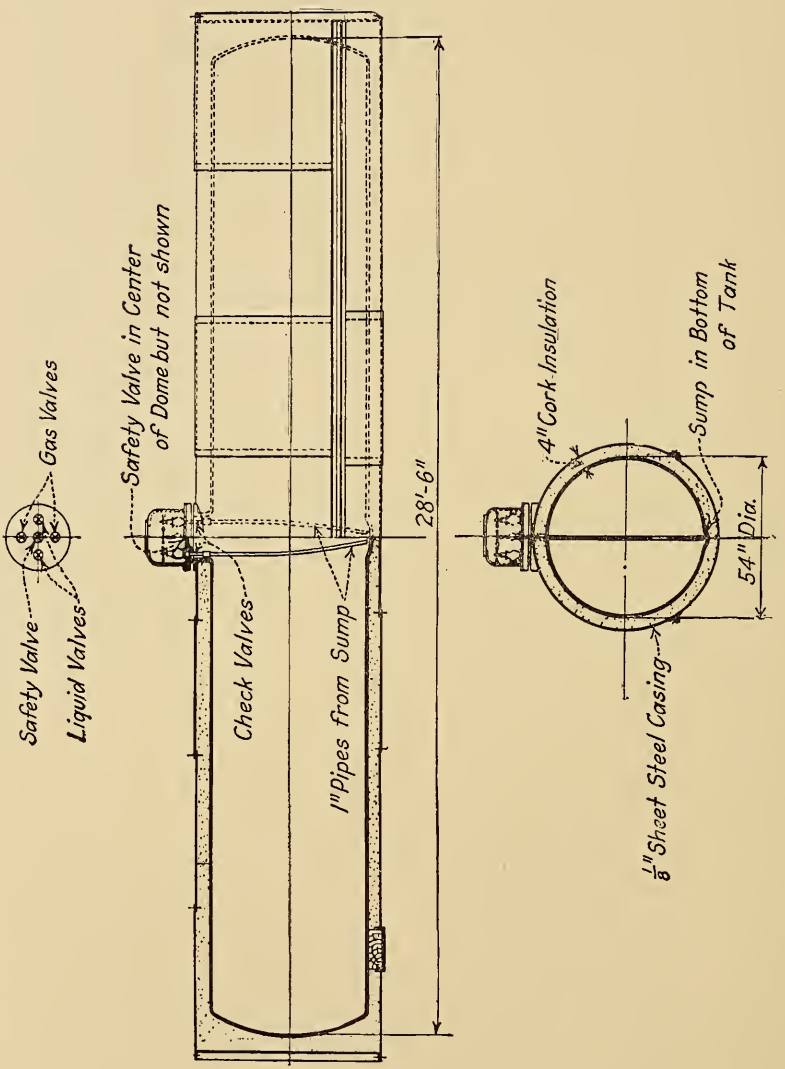

Safety Valve
Gas Valves
Liquid Valves
Safety Valve in Center of Dome but not shown
Check Valves
1" Pipes from Sump
28'-6"
4" Cork Insulation
Sump in Bottom of Tank
54" Dia.
1/8" Sheet Steel Casing

FIG. 3

The usual size of tank is 54 inches outside diameter by 28 feet 6 inches inside length between the heads, which allows for a lading of 30,000 pounds in compliance with regulations limiting the lading to 87 per cent of the gallonage capacity. Space is thus left above the liquid to provide for expansion of the contents due to rise in temperature, no dome capacity being provided for this purpose.

It may be interesting to remark at this point that a number of Class V tank cars have been in use in this country for twelve years and show no signs of corrosion.

Insulation.—The tank is completely covered with compressed cork board, 4 to 5 inches thick, and molded to fit its particular radius. The whole is then covered with a steel jacket ⅛" thick (Fig. 3).

Attention should be called to the fact that the Class V tank car is the only *insulated* chlorine container in use at the present time; further, that this feature is one of the greatest importance, especially in influencing the behavior of the container when exposed to the heat of adjacent fires.

In January, 1921, at the plant of the Lincoln Paper Mills Company, Limited, Merritton, Ontario, one of these insulated tank cars was located about 36 feet away from a one-story wooden building, 40 feet by 60 feet, filled with bales of scrap paper, when the building caught fire and was destroyed. Since the car contained 15,000 pounds of liquid chlorine, the superintendent's first thought was to move it out of the fire zone; however, he was unable to complete arrangements for doing so, and allowed the car to remain where it was. The shell of the car became very hot, just how hot we are unable to state; however, the superintendent reports that when the fire died down sufficiently to allow him to reach the car, the shell was still so hot that he was unable to hold his hand on it. Three hours after the fire started the mill began withdrawing chlorine from the car for the manufacture of bleach liquor, and the superintendent observed that the pressure in the tank car had risen but ten pounds on account of the fire. Under the conditions existing non-insulated containers equipped with fusible elements would certainly have acted much differently, and it is probable that some of the fusible elements would have yielded, allowing chlorine to escape into the mill yard.

Apart from its value in the case of adjacent fires, it is obvious that the insulation retards the rate of increase or decrease of internal pressure induced by changes in atmospheric temperature. Because

of the low specific heat of liquid chlorine (0.226), and the good heat-conducting properties of steel, the pressure in non-insulated chlorine containers responds quickly to changes in atmospheric temperature. A case has been observed where on an April afternoon in a northern climate the pressure in a ton drum exposed to the sun was nearly 200 pounds, while, after a cold night, the pressure was but 35 pounds the next morning.

The following table gives the rise in temperature and pressure of the contents of an insulated tank car during a period of 96 hours immediately following the loading of the car, from which it will be noted that the insulation is quite efficient.

Time.	Temperature Contents.	Change During Period.	Pressure.	Change During Period.
(Start)	(−9 deg. C.)	.....	(64 lbs.)	.....
End 24 hrs.....	−2 deg. C.	7 deg. C.	76 lbs.	12 lbs.
End 48 hrs.....	+3.5 deg. C.	5.5 deg. C.	88 lbs.	12 lbs.
End 72 hrs.....	+6 deg. C.	2.5 deg. C.	93 lbs.	5 lbs.
End 96 hrs.....	+8.5 deg. C.	2.5 deg. C.	98 lbs.	5 lbs.

NOTE: Average air temperature 17 degrees C.

It has been our experience that the hottest weather will not produce a pressure in the tank exceeding 160 pounds. In case of fires where extreme pressure might be developed, the safety valve will release at 200 pounds pressure, releasing gas only, and no liquid, and, of course, will shut off when the pressure drops below this point.

It may be of interest to relate an occurrence that will serve to illustrate the abuse that an insulated car of this type will stand. Several years ago it was the common practice at the plant of the Metals Chemical Co., Welland, Ontario, to draw gas from the car instead of liquid, and the usual way of keeping up the pressure during the winter months was to build a fire directly under the car, a practice which we did not know at the time and of which practice we certainly do not approve. After the fact was established an inspection was made of the cars subjected to this unusual treatment; however, we found that no damage had been done to the insulation or the surrounding shell.

Fittings.—The man-hole cover-plate is fitted with four 1-inch flanged cut-off valves (Fig. 4), a special gasket being used in a tongue

and groove joint. Two of these supply gas, while two connect with 1-inch eduction pipes leading to a sump, which makes complete emptying possible. The cover-plate is also fitted with one safety valve of an approved type, which communicates with the gas space only. The entire valve assembly is covered with a cast steel dome bolted to the cover-plate, the dome being provided with a screw-plate which affords easy access to the valves at the consumer's plant. Each time the car returns all cut-off valves are removed from the cover-plate to be refitted and tested, and an internal inspection of the tank made.

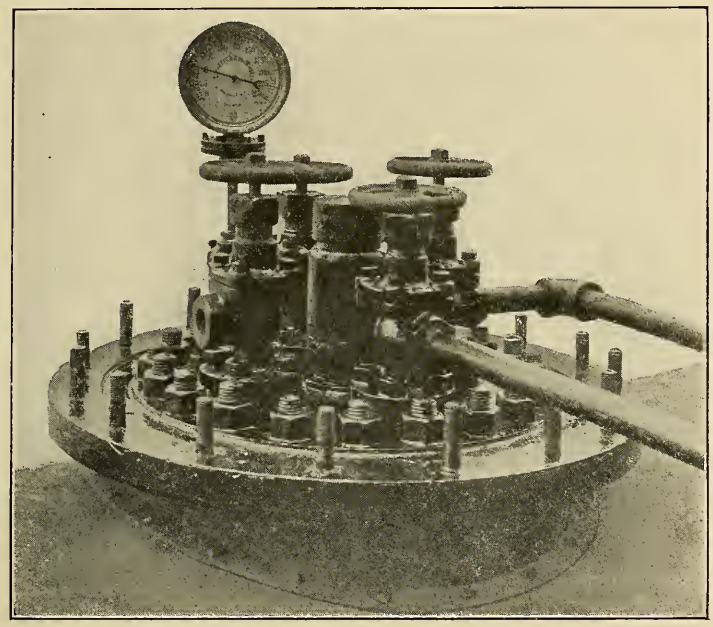


FIG. 4

Safety Fittings.—(*a*) *Safety Valve* (Fig. 5) : The car is equipped with a single safety valve, as mentioned above, which works on the principle of pressure applied against a coiled spring. This is tested and set to open at a pressure of 200 pounds per square inch, and is overhauled and reset at intervals of not over two years, according to regulations laid down by the Bureau of Explosives, to whom the design of the valve and its arrangement on the cover-plate was submitted for approval.

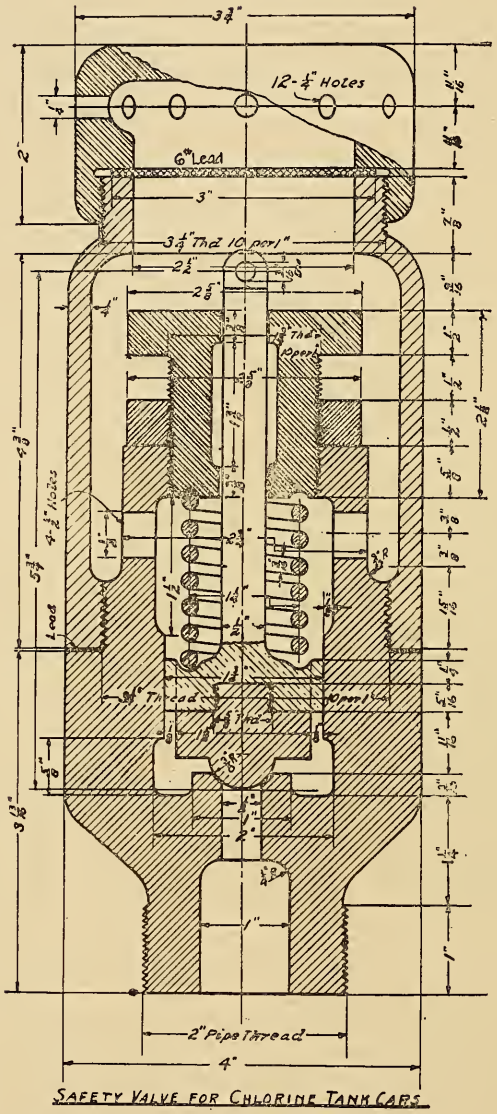

12-¼" Holes
6" Lead
3"
3¼" Thd 10 per 1"
2½"
2⅝"
4-½" Holes
Lead
Thread
2" Pipe Thread
4"
SAFETY VALVE FOR CHLORINE TANK CARS

FIG. 5

If the pressure in the tank exceeds 200 pounds, the safety valve opens and gas, not liquid chlorine, escapes, the valve reseating itself on the lowering of pressure. No other approved chlorine container has this particular type of safety element, and, in our opinion, the employment of this type of safety device in place of fusible elements, and the insulation feature, make this tank car the safest container from a fire standpoint.

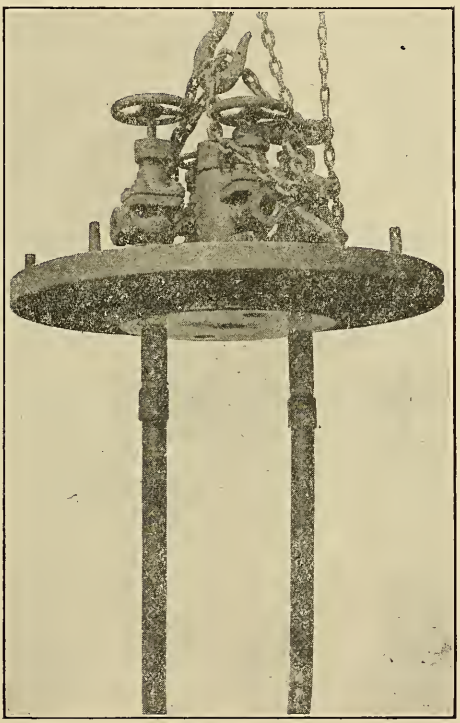


FIG. 6

(*b*) Another safety element, to which we will give more attention later, is the check valve (Figs. 6 and 14) located in the eduction pipes under the cover-plate, which makes the escape of liquid chlorine impossible if the cut-off valves on the eduction lines should be sheared off in a wreck.

Handling Tank Cars.—The car always rests on a track scale while being filled through one of the valves, and the weight is double

checked by weighing on a second track scale to make sure that the weight regulations are complied with. The customer usually checks the weight at his end by determining the amount of chlorine absorbed in his alkali solutions. In practically all cases the car is emptied

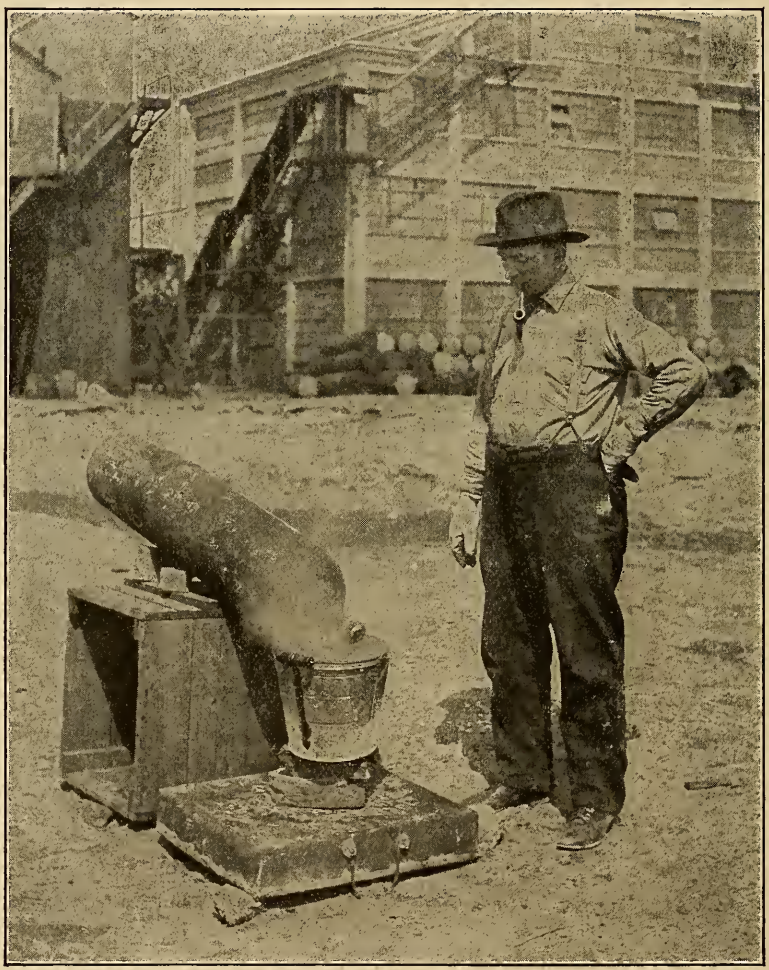


FIG. 7

through one of the eduction pipes and the liquid is led to an external evaporator to be gasified. In very cold climates the cars are run into warming sheds to hasten the unloading. These cars are either un-

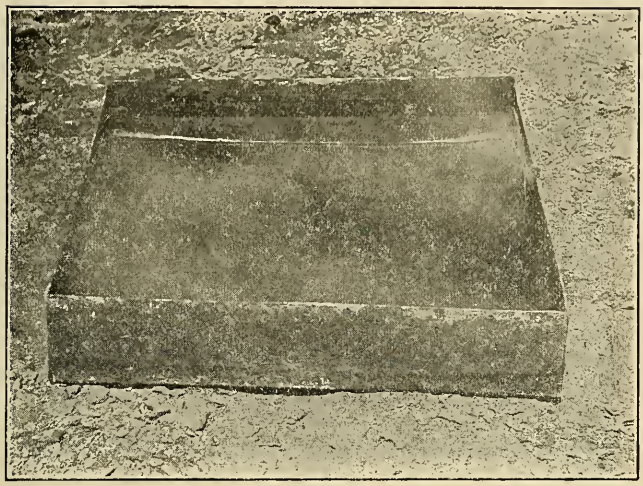


FIG. 8

loaded directly into the absorption system of the plant or the contents are drawn off into ton drums or fifteen-ton tanks for storage.

There are many inherent advantages in the use of a chlorine container of this size, just as there is in handling sulphuric acid in tank cars instead of drums or carboys. Aside from very material savings

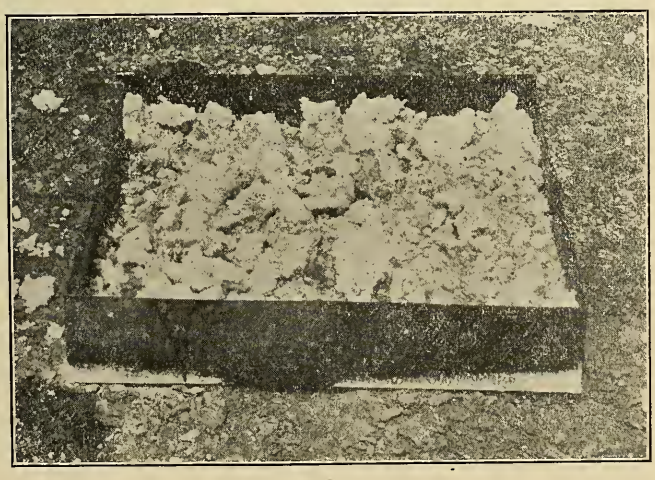


FIG. 9

in freight, there is a saving in labor at the consumer's plant for the reason that but one connection has to be made in unloading the car into the absorption system, which also serves to cut down the chances for annoying leaks.

FIG. 10

The manufacturer using large containers for the transportation of liquid chlorine has been asked repeatedly what should be done in case the car were wrecked and the liquid chlorine allowed to escape on the ground. In the first place, it should be recognized that the rate of evaporation of chlorine from a pool is much slower than one would assume from the nature of the element. This is shown in the photograph of an operator filling an open bucket with liquid chlorine drawn from a partially inverted cylinder (Fig. 7), and further by the photograph of an open pan of liquid chlorine exposed to direct sunlight (Fig. 8). After a thorough study of the situation the manu-

facturer has come to the conclusion that the best way to handle any large leaks of liquid chlorine is by pouring water on the pools. Chlorine hydrate is formed at once, which decomposes slowly, and this formation in a large measure eliminates the hazardous feature. The

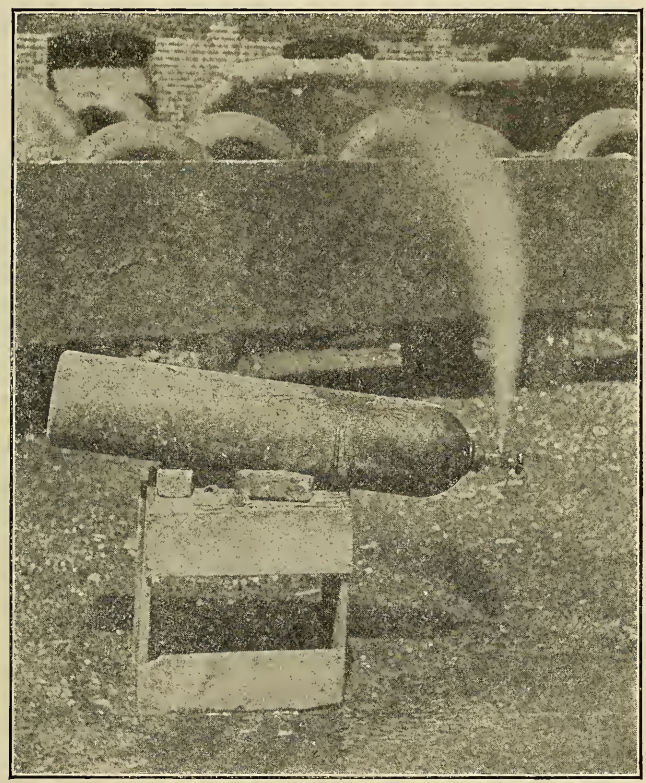


FIG. 11

effect of water on the liquid chlorine in the pan mentioned above is shown in Figs. 9–10, also the effect of playing a hose on a stream of liquid chlorine issuing from the open valve of a partially inverted cylinder (Figs. 11–13). In the case of very large pools, after water has been applied, earth or other like materials could be thrown over the chlorine hydrate, minimizing the evaporation. It is always possible to work on the windward side of a pool of liquid chlorine, and in the event no water was at hand, it would be possible to ditch the

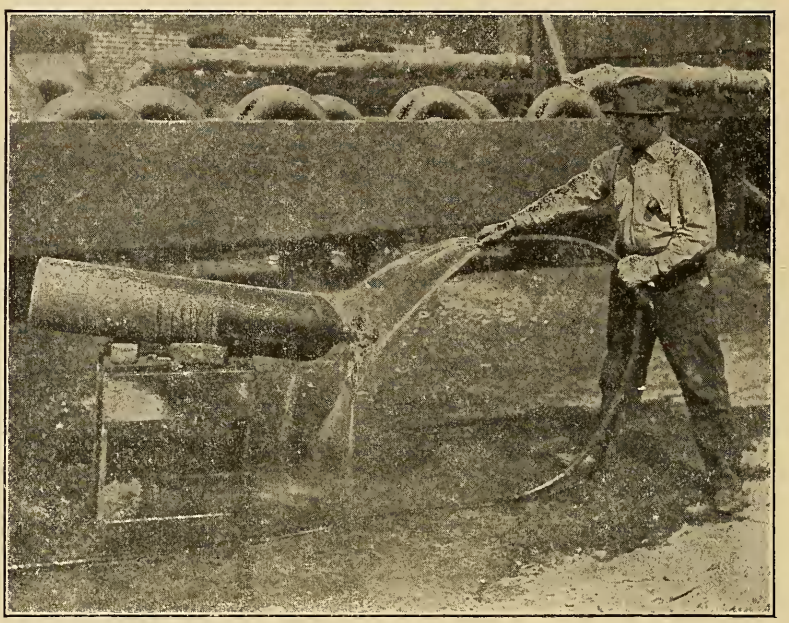


FIG. 12

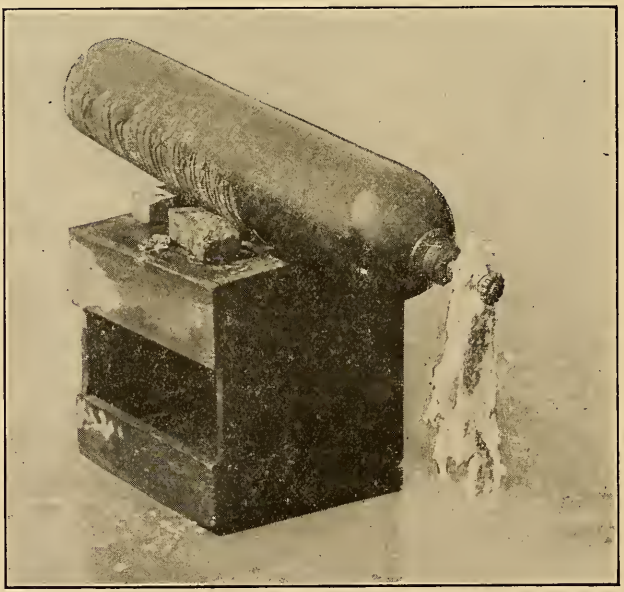


FIG. 13

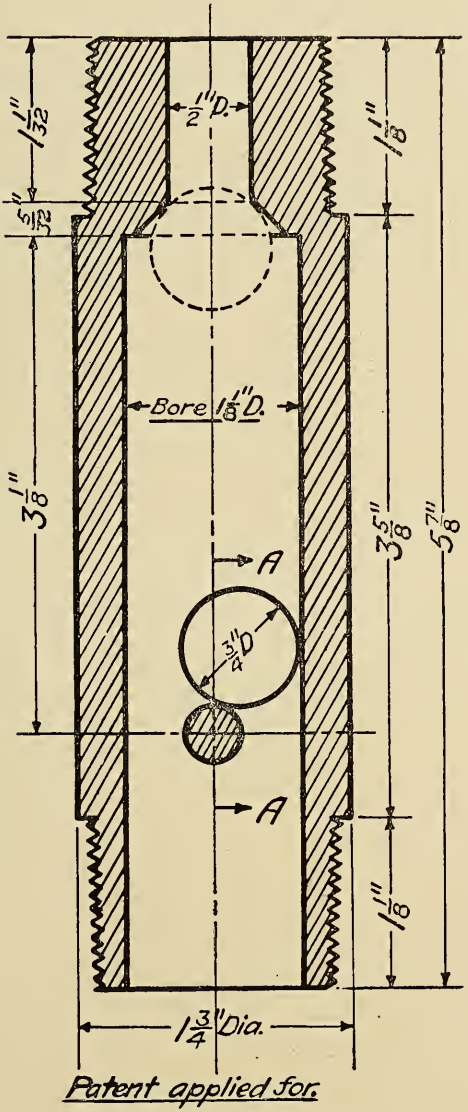

1/32"
5/32"
1/2" D.
1 1/8"
Bore 1 1/8" D.
3 1/8"
3 5/8"
5 7/8"
A
3/4" D
A
1 1/8"
1 3/4" Dia.
Patent applied for.

FIG. 14

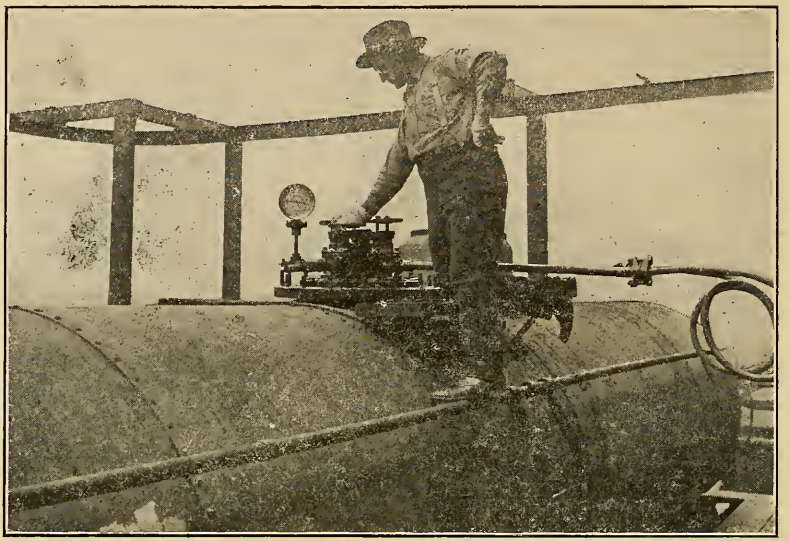


FIG. 15

chlorine to a near-by low spot and cover it with earth or similar material to hold back the evaporation.

In considering what will happen when a container of liquid chlo-

FIG. 16

rine is in a fire, experience goes to show that the upward draft will cause the chlorine to rise with the products of combustion, and that the fire fighters will not be inconvenienced. There are a number of cases on record where chlorine in considerable quantities was stored in buildings which took fire and the firemen never knew of its presence.

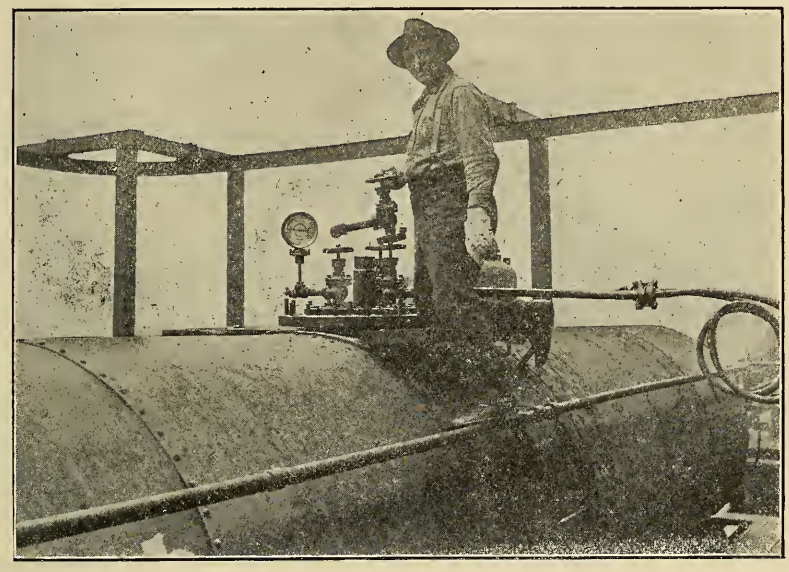
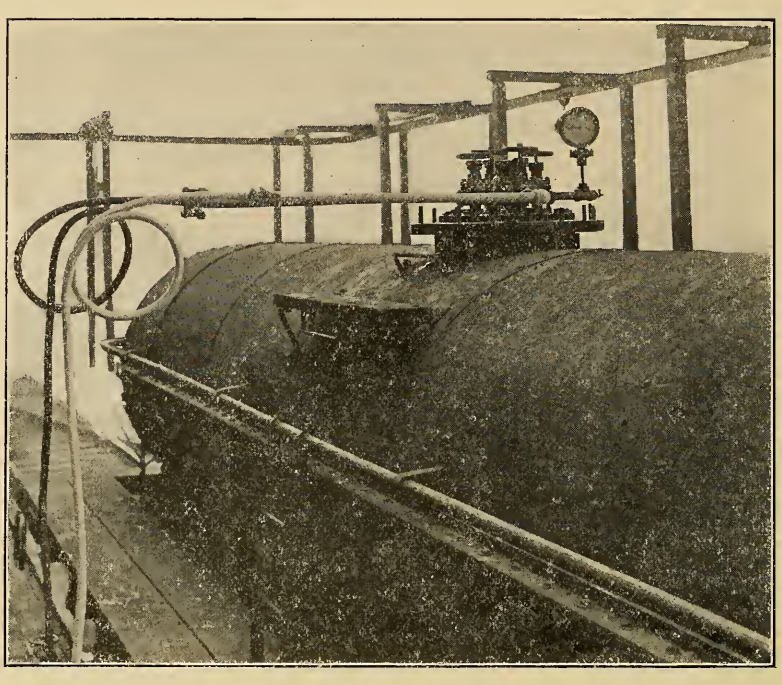


FIG. 17

Check Valve in Eduction Pipe.—It is obvious that the quantities required by the larger mills in the ordinary working day necessitate that the chlorine be withdrawn from the container as liquid and gasified externally in a liquid chlorine evaporator. This condition makes it necessary to equip major containers with permanent internal eduction pipes (Figs. 3 and 6), and at once brings up the question as to what would happen if the cut-off valves on such pipes were sheared off. In case a gas valve is sheared off the evaporation within the container will lower the temperature and consequently the pressure of the contents, and the rate of flow will lessen after the first rush. With a liquid leak, however, such conditions do not exist to the same extent, and our company has answered the question by designing a ball check valve which has been installed in the eduction pipes under the cover-plate in all the cars owned and controlled by the company.



Chlorine Tank Car During Filling—Note Frost on Filling Line

Tank Car at Unloading Shed—Customer's Plant

The check valve (Figs. 6 and 14) is a seamless monel tube about 1¾ inches in diameter and 6 inches long, counter-drilled on the interior to about three-fourths its length. At the top of this counter-drilling is an accurately machined seat which fits a monel ball placed within the larger diameter, the later being held in its normal position by a monel pin. The dimensions of this monel sleeve and ball have been so proportioned that with a flow of liquid in excess of 5,000 pounds per hour the ball will rise against the seat and cut off any further flow of liquid. With no back pressure existing, an opening of the valve wheel in excess of one turn will produce a velocity and volume of flow sufficient to seat the ball. We regard this as the outstanding safety feature of the car, and while this device can be installed in all cars of the Class V type, it would appear difficult to adapt it to any chlorine container not equipped with a man-hole to allow free access to the eduction pipe assembly. The efficiency of the ball check valve is shown in Figs. 15–17—an operator changing the liquid cut-off valve on a filled car without the need of a gas mask, and with no discomfort.

MULTIPLE UNIT TANK CAR FOR THE TRANSPORTATION OF LIQUID CHLORINE

By MAX MAURAN

Read at the Niagara Falls Meeting, June 22, 1922

In the summer of 1908 the writer went to Germany to investigate methods of liquefying, transporting, and storage of liquid chlorine. A number of plants were visited. The various methods of liquefying chlorine, as practiced in Germany at that time, are now in common use. Two methods of transportation were noted. Cylinders holding in the neighborhood of 100 pounds were being used, and small tank cars holding, if I remember correctly, about five tons of chlorine. As these cars were being used exclusively between the manufacturer's plant and one consumer, they could hardly be considered to be in general use throughout the country.

Comparatively very little liquid chlorine was being used in this country in the year 1908. It was thought by our company that, in order to promote and increase the use of liquid chlorine, cheaper methods of transportation, with due regard to safety, would have to be found. Tank cars similar to the German car were considered, but on account of the longer haul, with the consequent tying up of equipment, and the possible danger of shipping chlorine in such a design of car, they were not adopted. Cylinders holding 100 pounds were used, but in order to cut down the freight on containers versus contents, the writer designed a steel tank that would enable our company to transport liquid chlorine at a considerably lesser cost than by the use of cylinders holding 100 pounds. These tanks were designed to hold 2,000 pounds of liquid chlorine; they were 30 inches in diameter and about 6 feet long. They were constructed with a manhole in one end, to permit of periodical internal inspection. Valves were placed in the manhole cover with pipes connected thereto. These pipes project radially from the center of tank in opposite directions, so that when the tank was placed with the valves one above the other, either liquid or gaseous chlorine would be withdrawn from the tank. The tanks were tested to 500 pounds hydrostatic pressure per square inch.

A number of these tanks were built by our company, the longitudinal seams and the heads being welded into the tank by the oxy-acetylene method. They were loaded and shipped to various consumers.

The question of safety in the transportation of liquefied gases was brought up by the Bureau of Explosives in the year 1914, and in conference with the Bureau of Explosives and the manufacturers of the liquefied gases under discussion it was decided that for the shipment of liquid chlorine only seamless drawn cylinders, holding not over 150 pounds of liquid chlorine, should in the future be allowed. This ruling did not affect the use of tank cars, holding 15 tons of liquid chlorine, in spite of the fact that the tanks of these were constructed with welded seams. Their ruling, of course, eliminated the use of the so-called one-ton chlorine container, and our company was, in consequence, forced to abandon the use of same, limiting their shipments to cylinders holding 150 pounds, or to the use of tank cars.

The recent war altered all these conditions; when the chlorine manufacturers were called upon to deliver large quantities of liquid chlorine, it was found that the one-ton containers proved to be the most practical, all things considered, and several hundred were made and shipped, not only to consumers in this country, but also to France. On the strength of the experience gained during this period, our company petitioned the Bureau of Explosives, asking that they reconsider the question and allow us to ship in one-ton containers, in carload lots, from our plant to the consumers. This permission was granted, which resulted in the designing of a special car, known as the Multiple Unit Tank Car.

An important factor which influenced the adoption of the multiple unit type of car for the transportation of liquefied gas was the undeniable importance, as a safety consideration, of reducing to a safe point the quantity carried in one container. The many new uses being found for liquefied chlorine gas are creating an ever-widening area of distribution to the consumers, involving, on the part of the carriers, a far different transportation question than when the consumers were limited to a very few points of destination and the transportation service performed was over certain routes familiar by experience with the handling of this product.

We are convinced that a new factor must be considered—that is, the use of equipment that will make apparent, beyond all question, the nature of the commodity being transported, and will provide for

absolute safety, not only in transportation, but at the plant of the consumers, and while in the hands of employees of the carriers and the consumers not wholly familiar with the nature of the product they are handling.

In the final analysis it is certain that the railroad carriers are dependent upon the manufacturer and shipper of the product to devise such a means of transportation, one that will insure the greatest possible degree of safety; indeed, it is almost certain that the legal liability for any damages would ultimately lie with the shipper or the manufacturer in the event of any accident that could be attributed to a hazard resulting from an improper shipping container. In this respect the interests of the entire chlorine industry are one, and the results that would follow an accidental discharge of chlorine in quantity due to the use of any type of container or vehicle of transportation that might be proven hazardous would constitute a serious menace to the best interests of the industry as a whole.

With this in view, therefore, we felt obliged to assume that the best interests of the carriers were at one with our interests, and that it was our duty to take every precaution toward eliminating all foreseen hazards of transportation. This we have accomplished by the use of the multiple unit tank car where the individual unit carries a maximum quantity of one ton of liquefied chlorine gas, in a container that is fully inspected and cleansed before filling, the filling of which is carried out with absolute accuracy, and the exterior of which is at all times open to inspection. The individual unit is likewise safeguarded by the usual safety devices making it apparent that no conceivable accident could release the contents in a way seriously detrimental to the public safety.

In transporting tanks or drums of a material such as liquid chlorine it is important to provide that the tanks or drums shall be securely held in place, without danger of accidental removal from the car, or from motion of the car either transversely or longitudinally. If the drums or tanks are placed on end, with their axes vertical, the pitching and rolling motion of the car is exaggerated on the tanks. If a considerable number of tanks are horizontally arranged on the car, they will tend to move with the motion of the car, unless they are braced and stored with the greatest of care.

It will be noted from the drawing that the design of the car follows the standard steel underframe construction, the load being carried by the longitudinal box girder.

Its novelty consists in the design of the cradles in which the tanks are held in a fixed position on the car, the cradles being, in effect, part of the car frame proper. The method of clamping the tanks to

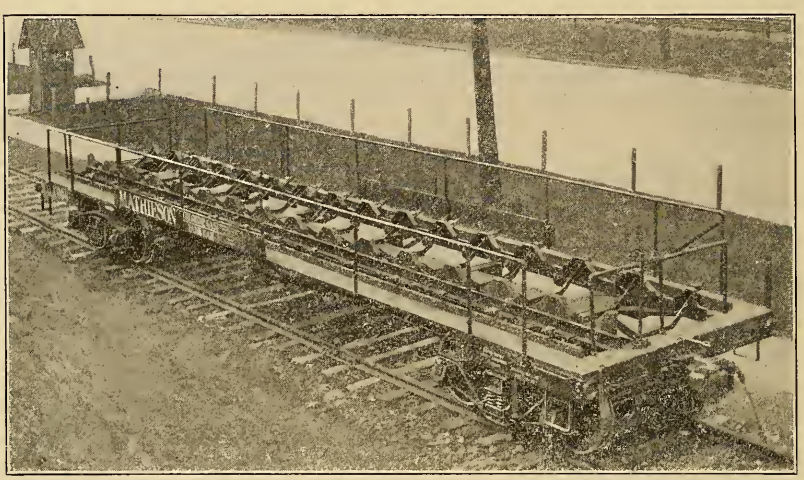


FIG. 1

the car frame or cradles prevents them from moving and rigidly secures them to the car. It will be seen that the usual car floor is dispensed with, runways being provided for the safety and convenience of the brakeman. In all other details the car follows the standard construction, in full compliance with tank-car specifications.

Unlike the first tanks constructed by our company, the tanks mounted on the special car do not have manholes placed in the end, as it was found by experience that these were unnecessary. The present tank is much stronger than the first tanks used by us. They have concave heads, forming a flange or chime at each end of the tank; these chimes are crimped inwardly, offering an excellent means for lifting the drums with chain hooks when loading or unloading them from the car. The construction of the chime also permits of the use of a specially designed clamp for holding the tanks to the car frame. These clamps consist of a threaded rod, hinged to the car frame at one end and carrying at the other a hook, which is moved along the rod in either direction by a flanged nut. A check nut is provided to prevent any possible movement of the hook after it has

been properly adjusted. In unloading the car, the check nuts are first loosened, the hook removed from the chime of the tank by the flange nut, the clamp is then swung away from the drums, allowing them to be freely lifted from the cradle. In loading the operations are, of course, reversed.

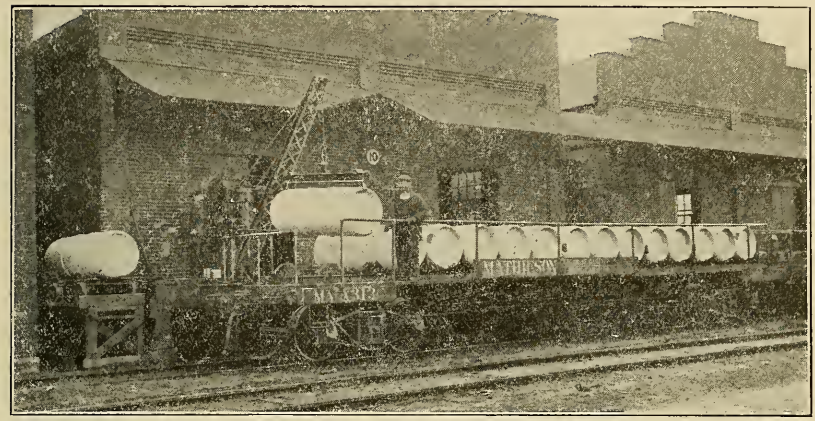
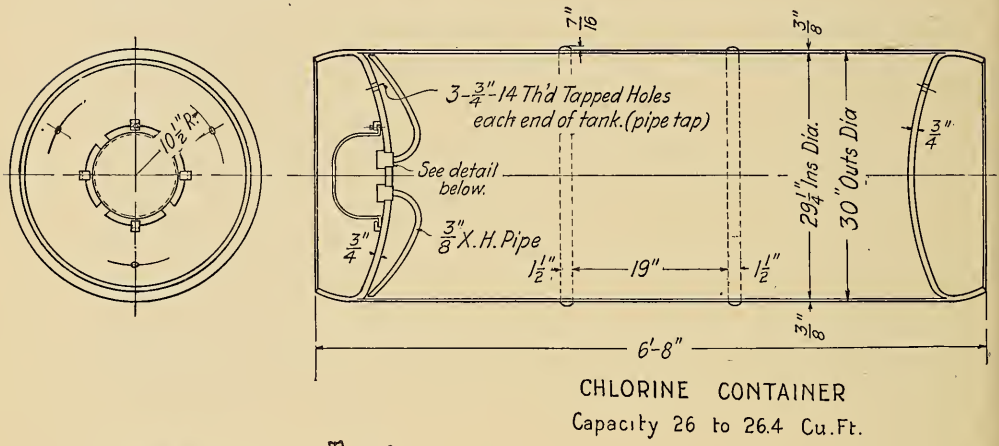


FIG. 2

The tanks can be unloaded without removing them from the car, by providing a header to which all the tanks can be connected. This header can be either placed on the car or installed at the localities where the car is to be unloaded. This method of unloading the car, however, is not recommended.

It is most important that the shipper shall know to an exactitude the amount of chlorine contained in each tank, and this is made possible by removing the tanks from the car and filling them while resting on sensitive scales. It is equally important that the consumer knows just the amount of chlorine he is obtaining. The use of a tank containing an exact weight of chlorine is highly important to the consumer, as it permits of chlorinating a predetermined charge, say, of a milk of lime solution, without the employment of a chemist or skilled operative. The tanks can be lifted from the car by a simple monorail hoist, conveyed to that part of the plant where it is intended to use the chlorine, or to a storage room. This permits of the car being rapidly unloaded and the empty tanks loaded and returned to the manufacturer for reshipment. This is of advantage, as it does not

necessitate the tying up of rolling stock or the payment of demurrage. It may be argued that, if customer leases his car, no demurrage charge will accrue. It follows, however, that if the customer keeps the car in his possession until all the chlorine is used up more equipment will be necessary, so that the consumer will have to pay the bill in either case. If the consumer's requirements are such that



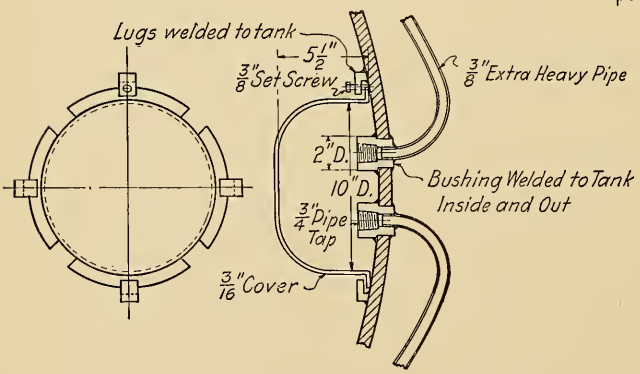


FIG. 3 FIG. 4

he can use the entire contents of a tank car before the time of limitation, he will, of course, be relieved from demurrage charges. He will of necessity, however, be compelled to put in storage tanks to take the contents of one, two, or more cars to tide him over any possible delay in transportation, and the writer considers it highly inexpedient to store liquid chlorine in tanks large enough to hold the contents of a full carload of liquid chlorine holding 15 tons.

The one-ton containers offer an excellent means for the storage of liquid chlorine by the consumer. On account of the turnover the consumer's storage tanks are constantly being examined and tested by the liquid chlorine producers' experts, assuring the consumer that all fittings in the way of valves, etc., connected to the tanks are in perfect working order, and that the tanks have not deteriorated in strength due to possible corrosion or change in the metal.

It is possible, and we hope in time to be permitted, to double tier the drums on our Multiple Unit Tank Car, which will permit the shipment of 29 tons of chlorine in one carload without undue risk, effecting considerable economies both to consumer and manufacturer.

The tanks are not covered with any insulating material, such covering the writer considers detrimental, as he has found by long experience that any steel surface subjected to moist chlorine fumes must be readily accessible at all times, so that the steel can be carefully protected from the action of the chlorine.

Discussion

Vice-President Smith: Is there any discussion of this paper?

Dr. Frerichs: Do I understand that this car loaded with 15 tons in one single-ton vessels is considered equivalent to a car carrying the same quantity in one single container?

Dr. Mauran: On account of its special design we think it is entitled to be called a tank car, the same as when designed with one tank, because the car is especially designed for that purpose alone and can not well be used for any other purpose. And with the tanks loaded and attached to the car it is in every sense the equivalent to a car carrying a similar quantity, but in a single container.

Dr. Frerichs: Is it considered by the railroad company to be a tank car?

Dr. Mauran: Not yet, but we hope to get that rule through.

Mr. Bacon: A thing I meant to ask somebody who is shipping chlorine: How much hydrochloric acid can you tolerate in chlorine? In Berlin I was told about shipping chlorine in tanks, and I was told that a very little hydrochloric acid turned over and over and over destroys the iron, and I was wondering how much was tolerated.

Dr. Mauran: Well, we don't tolerate any. The chlorine is practically 100 per cent. Traces of hydrochloric acid are sometimes found, but in the state in which they appear they have practically no effect on the container. There would be damage caused in some in-

stances, and that is one of our ideas in advocating the single container; the trouble is that in a great many of the chlorinating processes the operators do not watch the operation carefully. After the chlorine has been discharged from a tank, down to a point where the pressure is practically nil on the same, the remaining gas in the piping and container has a tendency to suck the solution back into the chlorine container, due to the vacuum formed by the absorption of the chlorine by the solution being chlorinated, so that it is often found that chlorine containers will be returned to the filling station with several pounds of foreign substance in them. So we make a practice of removing all cylinder valves from the containers as they are returned, for the purpose of inspecting the inside of the containers, washing them out, drying, and replacing the valves, so that when they again go out they are practically a new container. It is not practical to do this with a tank car holding 15 tons of chlorine in one tank.

DR. FRERICHS: I have heard the statement made that a small amount of water in the chlorine makes it highly dangerous. Is that true?

DR. MAURAN: We found when a certain amount was introduced that it would have an effect until after the action of forming iron chloride had been neutralized and would damage the cylinder to some extent. I do not know what amount of water would be considered dangerous in a liquefied chlorine. Certainly not the amount of moisture that would be found by careful liquefying; a small amount of moisture would have a certain effect.

DR. FRERICHS: The reference made was that chlorine hydrate would not affect or corrode iron. I should like to know whether there is any experience in that direction.

DR. MAURAN: I could not say as to that. Personally I have had no experience in that direction.

MR. BACON: Would water be quantitatively taken up as hydrate in case there was any water in there?

A MEMBER: I think that is a function of the temperature.

DR. MAURAN: I think not. I should think it would result in formation of HCl.

A MEMBER: I think the water there would attack a cylinder to form iron chloride.

DR. MAURAN: And hydrochloric acid.

A MEMBER: Yes; and until that became neutralized it would be at the expense of the interior wall of the container.

RECENT ADVANCES IN THE PRODUCTION OF PHOSPHORIC ACID FOR FERTILIZER AND FOOD PURPOSES

By WM. H. WAGGAMAN,

Scientist in Fertilizer Investigations,

Bureau of Soils, Washington, D. C.

Read at the Niagara Falls Meeting, June 22, 1922

Introduction.—The most extensively used chemical reagent to-day is sulphuric acid. There are very few industries in which this acid is not employed, directly or indirectly, in manufacturing the innumerable products so important to the comfort and convenience of the individual and essential to the progress of the nation. This acid has been aptly termed the "King of Chemicals," because without it most of our industries would be seriously hampered and some of them practically paralyzed. The other mineral acids which have rather wide industrial applications are nitric, hydrochloric, and phosphoric, but at the present time the manufacture of these acids is largely dependent upon sulphuric acid. Thus nitric acid, barring the small amount produced by the arc process and that obtained by the oxidation of ammonia, is chiefly manufactured by the action of sulphuric acid upon sodium nitrate. The bulk of our hydrochloric acid is obtained by treating chlorides with sulphuric acid, and nearly all of the phosphoric acid and soluble phosphates for fertilizer, food, and chemical purposes are produced by treating bones or phosphate rock with sulphuric acid.

It is obvious that it would be poor economic practice to employ these other mineral acids merely as reagents when their manufacture depends upon sulphuric acid, which is usually more effective, cheaper, and more readily handled and shipped. On the other hand, the chief function of sulphuric acid is that of a reagent, since it usually adds nothing of value to the material which it treats, while both nitric acid and phosphoric acid, besides having the power to effect certain chemical changes, carry in themselves marketable ingredients which add to the commercial value of the final product.

There is every indication, however, that in the future phosphoric acid is going to play a more important part in manufacturing processes than it has in the past, for the pyrolytic or furnace process of producing this acid has progressed to the point where industry has taken it up and the numerous chemical and mechanical difficulties involved are being gradually worked out. This method obviates the necessity of using sulphuric acid in the production of phosphoric acid direct from its compounds and has certain other attractive features which point to its wide adoption.

Advantages of Using Phosphoric Acid as a Reagent.—There are a number of advantages in the use of phosphoric acid rather than sulphuric and a number of conditions under which it may be more economically employed than the latter, provided, of course, that the cost of production is not too high. First, a number of elaborate and costly steps and factory manipulations, such as washing, screening, filtration, and evaporation, now necessary in the production of phosphates by the sulphuric acid method, would be materially reduced. Second, where sulphuric acid yields relatively valueless by-products, phosphoric acid produces only salable material, and hence the separation or handling and transportation of worthless filler or gangue would be largely eliminated. Ammonia for fertilizer and other purposes can just as well be fixed as ammonium phosphate as in the form of ammonium sulphate. Potassium chloride or muriate could be treated with phosphoric acid to produce potassium phosphate and hydrochloric acid as a by-product, and by the action of phosphoric acid upon Chile saltpeter or sodium nitrate we obtain nitric acid and sodium phosphate, both of which are marketable products. Third, we have in this country unlimited sources of raw materials necessary for the production of phosphoric acid by the furnace method, whereas we are importing large tonnages of pyrites from foreign sources to be used in the manufacture of sulphuric acid.

Phosphoric Acid for Food and Chemical Purposes.—While our main demand for phosphates in this country is for use in fertilizers, there is a large consumption of phosphoric acid in the manufacture of materials used directly or indirectly in food products. Thus phosphoric acid finds a wide application in the production of baking powder, self-rising flours, in the manufacture of jellies, preserves, and of soft drinks, and for medicinal purposes. The greatest consumption of phosphoric acid as such, however, is in the clarification of sugar

solutions and large quantities are annually used in the refineries of Cuba, South America, and this country.[1] It is also employed in rust-proofing paint, in the manufacture of salts of phosphoric acid for water softening and boiler scale compounds, and in a number of dental preparations. For most of these purposes a rather pure phosphoric acid is required, thus when acid is produced by the old standard method of treating phosphates with sulphuric acid very high-grade phosphate rock or bones must be employed. Acid of this character, of course, commands a premium over the less pure product employed in the manufacture of fertilizers.

Phosphoric Acid for Fertilizer Purposes.—Phosphate rock for fertilizer purposes does not have to be of the highest grade, but in manufacturing acid phosphate by the sulphuric acid process it is necessary to limit the amount of such impurities as iron and alumina, in order to obtain a product which will answer the availability tests set by the State fertilizer laws and at the same time be in a mechanical condition which will admit of its ready application to the soil. Therefore, even in the manufacture of acid phosphate many grades of phosphate rock are barred, either because of their low phosphoric acid content or the presence of abnormal quantities of aluminum and iron oxides which render them unfit for sulphuric acid treatment. In spite of these requirements, however, the phosphoric acid in fertilizers must be cheap in order to insure their wide application and enable the farmer to obtain increased yields at a price warranting their use.

Sulphuric Acid Method of Producing Phosphates and Phosphoric Acid.—The process of manufacturing soluble phosphoric acid by means of sulphuric acid is a familiar one. It consists of treating phosphate rock with an equal quantity of sulphuric acid and allowing this mixture to stand until the reaction is practically complete and the tricalcium phosphate is converted into monocalcium form. The average grade of phosphate rock used for manufacturing acid phosphate contains 32 per cent of phosphoric acid and the product obtained by sulphuric acid treatment contains 16 per cent of soluble phosphoric acid. If sufficient sulphuric acid is added, we obtain phosphoric acid which may be filtered, concentrated, and then used to treat phosphate rock in the production of double acid phosphate, containing from 40 to 50 per cent of soluble P_2O_5, and this product is made in Europe,

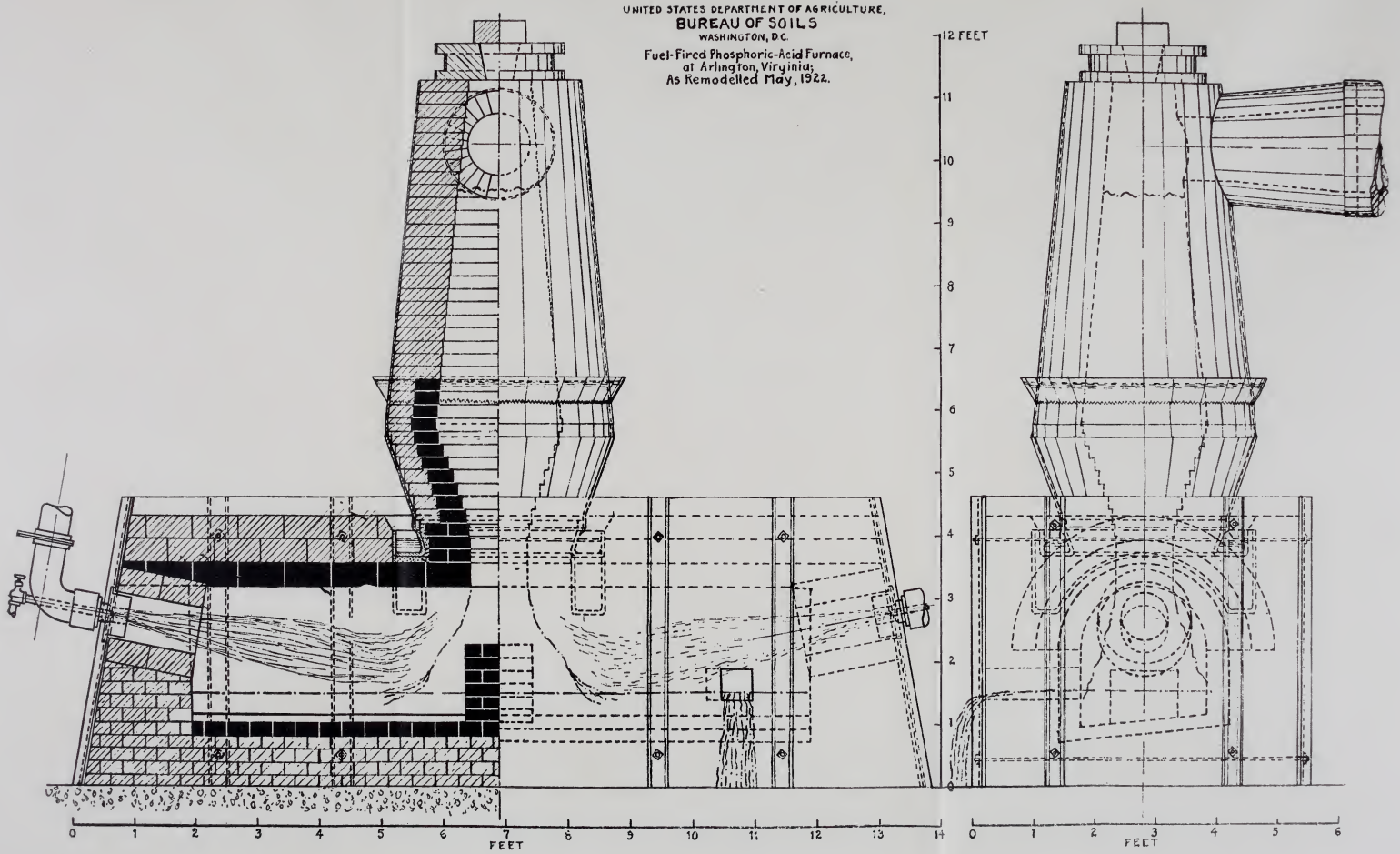
[1] Meckstroth, J. T., "Industrial Uses of Phosphoric Acid," *Chem. Met. Eng.*, 26, 223, (1922).

and to a certain extent in this country, in order to utilize relatively low-grade phosphate deposits which would give a dilute product if manufactured into acid phosphate direct. But whether ordinary acid phosphate is produced by direct treatment of sulphuric acid, or double acid phosphate is the product indirectly obtained, there are certain objections to manufacturing soluble phosphate by means of sulphuric acid. Ordinary acid phosphate is at its best a relatively low-grade product, the highest on the market seldom containing over 18 or 20 per cent P_2O_5. Double acid phosphate produced by the sulphuric acid process involves filtration and evaporation which largely offset the advantages gained in obtaining a concentrated product. In either case a reagent is employed which adds no fertilizer value to the final product and must be manufactured at or hauled to the fertilizer plant and hauled away again either within the fertilizer itself or disposed of as gypsum, which has little or no market value. The direct production of phosphoric acid by a furnace method wherein silica is employed in lieu of sulphuric acid offers many advantages, provided, of course, that the cost of the fuel or energy required to produce the unit of phosphoric acid is no greater than the cost of the sulphuric acid necessary to effect the same results. In fact, the pyrolytic process may still be more economical than the sulphuric acid method should the fuel or power costs be appreciably higher, since the raw materials used can in certain respects be much lower in grade and consequently cheaper, and the product obtained is so concentrated that transportation and handling charges per unit of phosphoric acid are materially reduced.

The Pyrolytic Method of Producing Phosphoric Acid.—Although the furnace method of producing phosphoric acid has only assumed much prominence within recent years, it is by no means a new process. Apparently the substitution of silica for sulphuric acid so that phosphorus could be produced directly from phosphates of lime was first proposed by two Frenchmen, Auberton and Boblique,[2] in 1867, when these inventors took out a patent for volatilizing and collecting elementary phosphorus from mixtures of phosphate rock, sand, and coke heated to a high temperature in closed containers. Ruymbeke[3] appears to have been the first in this country to patent the furnace process for the recovery of phosphoric acid rather than phosphorus. This

[2] Readman, J. B., *J. Soc. Chem. Ind.*, *9*, 473 (1890).

[3] U. S. Patent No. 540,124 (1895).


UNITED STATES DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS
WASHINGTON, D.C.
Fuel-Fired Phosphoric-Acid Furnace,
at Arlington, Virginia;
As Remodelled May, 1922.
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patent was taken out in 1895 and the inventor advocated the use of a blast furnace for this purpose. Although the manufacture of phosphorus in the electric furnace was generally adopted both in this country and abroad, the manufacture of phosphoric acid in this way received comparatively little consideration, and it was not until a plant of semi-commercial size was put into operation at Mt. Holly, N. C., operating under the Hechenbleikner patents, that commercial concerns began to evince an interest in this method.

The Bureau of Soils undertook investigations along these lines in 1916 and installed a simple electric furnace of semi-commercial size at Arlington Farm, Virginia. After considerable preliminary work it was found that while complete elimination of phosphoric acid could be readily brought about in this way, the complete collection of the volatilized acid required such elaborate absorption systems that it was desirable to employ a simpler method of recovering the product. Accordingly, Dr. W. H. Ross[4] of this Bureau decided to try out the Cottrell method of precipitation for collecting the volatilized acid, which worked so admirably and had such distinct advantages over the water absorption system that it was later adopted by the first large commercial plant producing phosphoric acid by the furnace process, namely, that of the Federal Phosphorus Company. The preliminary work at Arlington Farm, Virginia, made it seem desirable to carry this work further, so a co-operative arrangement was entered into with several outside concerns and a larger and better equipped plant was erected near the factory of R. B. Davis Baking Powder Company, at Hoboken, New Jersey. This experimental plant was in direct charge of Mr. J. N. Carothers, who, after the work was completed, resigned from the Bureau of Soils to take a position with the Federal Phosphorus Company mentioned above.

Mr. Carothers' figures,[5] obtained after several months, showed that P_2O_5 could be produced at a cost of 3.39 cents per lb., exclusive of interest, taxes, and depreciation charges. This figure, I believe, has since been reduced in actual commercial operation. As pointed out by this investigator, however, the furnace was of very simple design and had no regenerative features or means for utilizing the heat of the effluent gases, which should decrease appreciably the cost of production. By using, however, the concentrated acid collected by

[4] *J. Ind. Eng. Chem.*, 9, 26, (1917).
[5] *J. Ind. Eng. Chem.*, 10, (1918).

the Cottrell precipitator to treat another batch of phosphate rock, thus producing double acid phosphate, the final cost of the unit of soluble P_2O_5 would be materially reduced from that given above.

Use of Mine-Run Phosphates.—There is another very important factor, however, in the economic production of phosphoric acid by the furnace method which was not given much consideration in the earlier investigations, namely, that of using lower grades and run-of-mine phosphates which are inherently unfit for the manufacture of acid phosphate or must be separated from their impurities by an elaborate screening process which adds materially to their cost. With this in mind the writer undertook a number of experiments wherein run-of-mine phosphates from Florida and Tennessee were smelted in the electric furnace, sufficient sand being added to give the proper silica-lime ratio best adapted for the elimination of the phosphoric acid and the production of molten slag. It was found that such phosphates could be advantageously employed, provided, of course, they did not have to be hauled such long distances that the freight upon the silica and other impurities present would offset the advantages gained in the utilization of these lower grade materials. These investigations brought up another point which led to the work now being conducted by the Bureau, namely, whether fuel such as oil, coal, or coke could be employed in lieu of the electric arc for obtaining the necessary temperatures and evolution of phosphoric acid, for the phosphate deposits of Florida, as well as a number of those in Tennessee, are rather remote from sources of cheap hydroelectric power which would make it possible to utilize the electric furnace for the production of fertilizers. Accordingly, experiments were undertaken to see if the complete volatilization of phosphoric acid could not be brought about at the temperatures and under the conditions attained in a fuel-fired furnace. Much of this work has been published, but a short review here will probably be helpful to those interested in the subject.

The Use of the Fuel Furnace.—The first work was conducted with relatively pure samples of tricalcium phosphates, quartz flour, and carbon in open and closed graphite crucibles. Various proportions of these ingredients were heated in a small dental furnace employing city gas and an air blast which enabled us to obtain temperatures up to 1,600° C. The results showed conclusively that complete elimination of phosphoric acid could be obtained provided reducing conditions were maintained and sufficient silica were added to produce

a molten slag. Higher proportions of silica gave a more ready evolution of phosphoric acid. The proportions used as a result of this preliminary work were silica 39 per cent and lime 61 per cent.

The work was then conducted on a larger scale, and after several small furnaces were built and indirect heating employed it was decided to use fuel oil as a heating source and have the burning fuel in direct contact with the phosphate charge. The complete utilization of the fuel and the maintenance of reducing conditions, however, are rendered difficult where oxidation is depended upon to furnish the necessary heat units, and this, coupled with the fact that the run-of-mine phosphates of Florida are largely in small nodules mixed with finely divided phosphate, clay, and silica, made it necessary to adopt some means by which the carbon or coke present would not be oxidized while the phosphate mixture was being brought to the high temperature required. The plan finally adopted was to briquette the mixture, and after a good deal of preliminary investigation, wherein various binders were employed, it was found that the finely divided phosphate and clay present in many of the deposits of Florida and Tennessee was ample to bind the mixture into briquettes which stood up excellently on furnace treatment. The form of furnace which was used in these semi-commercial tests and the modified furnace which is now being employed is a combined blast and open-hearth type wherein the briquetted charge is fed down through a central shaft into an elongated crucible. Two oil burners, one at either end of this crucible, play their flames over the molten slag and up through the shaft, preheating the charge as it melts and runs down upon the hearth. Near the top of the furnace shaft a brick-lined flue leads into a dust catcher, and from the dust catcher the phosphoric acid and other gases are led into stoves similar to those used in ordinary blast furnace practice, where the combustible gases, consisting chiefly of CO, are burned, so that nothing but oxidized products are transmitted to the precipitator. An exhaust fan draws the gases from the stoves into the precipitator. The electrical treater consists of 9 six-inch terra-cotta pipes of seven lengths each, giving a total height of effective precipitating surface of 14 feet. This precipitator, although simple in design, has proved quite effective in collecting the acid, even though the velocity of the gases is somewhat greater than that ordinarily advised. Owing to insufficient funds and our limited personnel, we have experienced a great many mechanical difficulties in run-

ning this furnace, but these are gradually being ironed out and it is hoped that before the summer is over we will have sufficient data to warrant a better and larger installation. The longest run which we have made in this particular type of furnace is 20 hours, and during this time the furnace was only operating efficiently toward the last of the test. It is difficult to draw conclusions as to the cost of operation in a test of such short duration, but an approximation has been made, based on the last few hours of the run, which indicates that phosphoric acid (P_2O_5) can be produced by the fuel furnace process at 2½ cents per pound, including interest, taxes, overhead and depreciation charges. As pointed out before, the use of this acid for treating further batches of phosphate rock in the manufacture of double acid phosphate would materially reduce the cost of soluble P_2O_5.

Electric Versus Fuel Smelting.—The limited data so far obtained are insufficient to permit of a strict comparison between electric and fuel smelting of phosphate rock, but since the function of the electric furnace is merely that of supplying the requisite heat energy, it would seem that if the necessary temperatures can be attained by means of fuel (which our investigations have proven is perfectly feasible) the cost of a unit of P_2O_5 made by the fuel-fed furnace process should be materially lower than that obtained by the electric furnace method, unless electric energy is available at a price much lower than that prevailing at the present. In the following table there is shown the equivalent cost of the heat unit obtained by fuel as compared with that furnished by electric energy, at various prices per hp. year:

This table shows very conclusively that the actual cost of the heat unit produced by various fuels is far below that at which it may be furnished by electric power unless a project, such as that at Muscle Shoals, is developed. It is not altogether fair, however, to compare the efficiency of the two methods on the basis of the cost of the heat unit furnished by each. In the electric furnace the heat is very much localized and there is much less loss through radiation and in the effluent gases than in a furnace process where excess air must be introduced for the combustion of the fuel. By proper regenerative apparatus and means of utilizing the sensible heat in the effluent gases, however, this loss of valuable heat units may be materially reduced. The shaft type of furnace, therefore, whether used in connection with electric smelting or fuel smelting, appears, if properly designed, to be the logical apparatus to employ in the production of phosphoric acid

by the pyrolytic process. Mr. George T. Southgate, formerly with the American Cyanamid Company, is now temporarily employed by the Bureau of Soils designing a shaft furnace of semi-commercial size which may be adapted to burning either coal, coke, or fuel oil.

TABLE I

PRICES ASSUMED FOR ELECTRIC POWER AND CORRESPONDING COSTS OF STANDARD FUELS AS SOURCES OF EQUIVALENT QUANTITIES OF HEAT

Electric Power Cost per K.W. Yr.	Corresponding Cost of Standard Fuels Delivering Equivalent Amount of Heat			
	Coal per ton	Fuel Oil per gal.	Coke per ton	Natural Gas per M cu. ft.
Dollars.....	Dollars	Cents	Dollars	Dollars
5.00.....	4.60	2.4	4.60	20.00
10.00.....	9.20	4.8	9.20	40.00
15.00.....	13.80	7.2	13.80	60.00
20.00.....	18.40	9.6	18.40	80.00
25.00.....	23.00	12.0	23.00	100.00
30.00.....	27.60	14.4	27.60	120.00
35.00.....	32.20	16.8	32.20	140.00
40.00.....	36.80	19.2	36.80	160.00

To offset the greater efficiency of the electric furnace in utilizing heat energy, it may be said that at present the productive phosphate fields are hardly sufficiently close to electric power sites to allow the use of run-of-mine phosphates because of the freight charges on a large amount of relatively valueless material, which, though necessary to bring about the furnace reactions, does not add to the value of the product. Fuel oil in Florida, on the other hand, and coal and coke in Tennessee are relatively cheap and therefore a furnace plant might well be erected at the phosphate mines where there are unlimited phosphate resources and concentrated products could be shipped direct from the source of the raw material. With the development of Muscle Shoals, however, power could be transmitted to certain of the phosphate fields of Tennessee at a relatively low cost, since some of these deposits are within 50 to 60 miles of Florence and Sheffield, Alabama. It is quite possible that a combination of the fuel and electric furnace may eventually be employed.

It has been stated earlier in this paper that it might well be possible to have the cost of fuel or electric power necessary to produce a unit of phosphoric acid greater than the cost of the sulphuric acid

necessary to effect the same result. This is particularly true as regards fertilizer because of the enormous saving which would be effected in shipping the phosphate product. Under normal conditions our annual production of acid phosphate is approximately 4,000,000 tons. Of this amount, only 16 per cent, or 640,000 tons, is phosphoric acid (P_2O_5). The average freight on acid phosphate is $3 a ton, so we are paying $12,000,000 a year for shipping phosphate material 84 per cent of which is relatively valueless. Assuming, now, that we produce double acid phosphate containing 48 per cent of P_2O_5 instead of ordinary 16 per cent acid phosphate, we would have the same quantity of marketable ingredient in 1,280,000 tons instead of 4,000,000 tons of product. This difference of 2,720,000 tons, at an average price of $3 per ton for freight, would mean a saving of $8,160,000 annually. Fertilizer companies which purchase their acid from outside sources have to pay the freight on sulphuric acid both to and from the factory, and this double charge would be eliminated where the furnace process was employed.

Conclusion.—As far as the production of very pure phosphoric acid for food and chemical purposes is concerned, there is little question that the pyrolytic process is superior to the sulphuric acid method. In the manufacture of phosphates for agricultural purposes, however, the pyrolytic process is not sufficiently far advanced to be a factor. But the time is not far distant when it will at least prove a valuable adjunct to the older and more generally employed method.

Even under the most favorable conditions, however, the use of concentrated phosphates for fertilizer purposes and the replacement of acid chambers by phosphate furnaces will come about very gradually, for the American farmer has grown accustomed to relatively low-grade materials and acid phosphate has up to the present satisfied his requirements. Moreover, in many manufacturing processes where a cheap reagent is required only for its acid or dehydrating properties it would be poor economic practice to use phosphoric instead of sulphuric acid. The demands of these industries are such that we must always produce large tonnages of the latter acid.

But where the use of phosphoric acid actually adds market value to the product, as it does in the case of fertilizer, it is logical to employ it, and also highly desirable to produce it from its compounds by a more direct method than by the sulphuric acid process. Cheaper production and more efficient and economic distribution are equally

important to the mine owner, the manufacturer, and the agriculturist. The opportunity of prolonging the life of his phosphate deposits by utilizing them more fully than heretofore will appeal to the business sense of the average owner of phosphate property and the great saving in freight charges will prove attractive to the fertilizer manufacturer. The pyrolytic process, we believe, will eventually enable the latter to produce fertilizers more economically and to offer his product to the farmer at a lower price.

Discussion

Vice-President Smith: This paper is open for discussion.

Dr. Marshall: Because of my connection with the manufacture of fertilizer I have been very greatly interested in Mr. Waggaman's paper, particularly in his discussion of cost by the process he described. I might say that to-day in the Baltimore market acid phosphate is quoted on the basis of 2½ cents per pound P_2O_5. In other words, to-day's quotation, with the present high labor charges, high freight rates, and before the 10 per cent reduction in freight, shows that the cost of manufacture by the sulphuric acid process is about the same as the best result Mr. Waggaman's process could develop. I think Mr. Waggaman's figures must be on the high side, as otherwise his method would have no possibility of competition with acid phosphate made by the regular process.

Another point I desire to make is with reference to the transportation charges. You can not ship phosphoric acid itself as a fertilizer. If you want to make any comparison, you must make a comparison with the shipment of a phosphate salt. In other words, instead of shipping 84 per cent of inert material, you have got to assume that in any ordinary fertilizer made with sulphuric acid you are shipping 60 per cent of inert material instead of 84.

Mr. Waggaman: These figures on the cost of production are, of course, partly assumed and based on the prices of labor and materials prevailing over a year and a half back. I have not revised them since the price of labor and fuel oil dropped.

Mr. Marshall: You spoke of shipping 84 per cent inert material?

Mr. Waggaman: Ordinary 16 per cent acid phosphate is the usual carrier of phosphoric acid, but you can carry the same amount of phosphoric acid in much smaller bulk in the form of double superphosphate which contains from 45 to 50 per cent P_2O_5.

DR. CARRUTHERS: The Government said the cost of production was 3.39 cents per pound, if I remember it correctly, and I would like to ask you what that figure was based on, in regard to phosphate rock price.

MR. WAGGAMAN: I believe Mr. Carruthers can give you data from his experiments on the electric smelting of phosphate rock better than I. He is familiar with it. I think if you put in any investment charges or overhead charges that they will considerably increase the cost. There is also the question of the high price of rock prevailing at the time of his experiments. Can you not give us figures on that, Dr. Carruthers?

DR. CARRUTHERS: I am not positive. My recollection is that it is $8 on rock and $6 on coke. The labor is, of course, an important item.

MR. MARSHALL: I might say that the current figures in Baltimore are based on sulphuric acid at $8 and rock at $5.80, these being the prevailing market quotations.

DR. LANDIS: I have not much to add to this from a technical standpoint; from a commercial standpoint many factors have been left out of the reports on the smelting of phosphate rock. I have been interested in the subject for twelve years and have carried on quite large scale experimental work. The early experiments used rotary kilns. The scale of operations, though quite large, yielded nothing encouraging. The next set of experiments were based on preliminary work nearly one hundred years old. Our attempts failed purely on construction details, and our later repetition through 1910 and part of 1912 fell down from the same cause. It is not at all a question of process, but a question of practical application, and I have not seen in any of the estimates presented any adequate figures whatever on the item appearing to me to be the key to the whole situation.

In the set of experiments carried out in the rotary kiln we established the very important principle that the use of silica in this process can be made to displace phosphoric acid to a large extent. Although there has been very little work done on this phase by others, a very important influence on the process is exerted when direct replacement of a very large proportion of phosphoric acid is accomplished without the necessity of reduction. It takes many times more thermal energy to reduce the phosphate than to evolve through replacement

with silica. The effect on the thermal requirement is so great that we have never in our experimental work used anything like the energy called for in these estimates. Energy is not a large factor if you can get vaporization without the necessity of reduction. It is not necessary to have $5 power. Our problem is to get a refractory that will stand up. I have never seen any of the actual work which Mr. Waggaman has been carrying on. I have, however, seen photographs, and I think we will all recall the publications showing, after a few hours' run, the furnace badly burned out. Whether that is generally true or not, I do not know, but that follows my experience.

Now, the electric furnace itself offers a solution of this refractory problem, which is much more important than the energy question.

SOME NEW PETROLEUM PRODUCTS

THE VAPOR-PHASE, LOW-TEMPERATURE, CATALYTIC OXIDATION OF FUEL OIL AND OTHER CRUDE PETROLEUM FRACTIONS IS SHOWN TO YIELD A SERIES OF NOVEL CHEMICAL PRODUCTS WHICH APPEAR TO HAVE A BROAD RANGE OF POSSIBLE INDUSTRIAL APPLICATIONS.

BY J. H. JAMES

Read at the Baltimore Meeting, December 9, 1921

Very little chemistry enters into ordinary petroleum refining, the process on the whole being based on physical principles. Where chemistry is introduced at all, as in acid agitation or sulphur removal by the Frasch and other processes, it is only for the purpose of removing certain substances, the presence of which impairs the value of the main product. The "cracking" processes developed in recent years are, however, an exception to the foregoing statement, for they involve chemical changes. The various commercial products of petroleum in present-day practice are those mixtures of hydrocarbons the sum of which made up the greater part of the original crude.

The purpose of this paper is to describe in rather brief outline some work done in an attempt to prepare certain new chemical products by starting with petroleum as the raw material. The industrial application of the products thus obtained appears to belong in part to the oil industry and in part to industries decidedly remote. The fundamental idea of the process involved is the vapor-phase, low-temperature, catalytic oxidation of the aliphatic hydrocarbons of the petroleum.

While references are numerous in the literature to the many attempts made to oxidize petroleum hydrocarbons in the liquid phase, the first recorded work in the vapor phase appears to have been that of Walther.[1] Walther's apparatus, his arrangement and selection of catalysts and his temperature (he worked at a glowing red heat), as well as his air ratio (which must have been very high, as he main-

[1] Brit. Pat. 21,941 (1905).

tained self-sustained combustion), all show, as our experiments have proved, that his proposed process was bound to be a failure. In the one experiment cited in his patent, he claims to obtain a liquid of lower boiling point than the original material treated, although his description of the other products is noticeably incomplete.

Selection of Catalyst and Temperature Control

The author has found that the first requisite for success in obtaining yields sufficiently high and of satisfactory quality for industrial use is the selection of the catalyst. In this connection the oxides of certain metals of high atomic weight and low atomic volume, such as molybdenum and uranium, appear to be the most promising. Where compounds of closely related metals can be formed, such as diuranyl vanadate, very good results were obtained.

Numerous experiments have shown that many oxides have catalytic activity in this connection, but it is believed that for commercial development, all things considered, the best selection is within the group noted above. Good results have been obtained by passing the mixture of hydrocarbon vapor and air through a thin layer of uranium oxide and then on through two layers of catalyst consisting of the oxides of molybdenum. The reason for the three catalytic layers, or, as we call them, "catalytic screens," will be noted later. The uranium oxide is used in the first screen because this oxide has the specific property of catalyzing to a marked degree the aldehydic stage of oxidation, so that where acids are desired as the main product, this preliminary step brings about a higher yield of acids, the aldehydic bodies going over to acids in the second and third screens.

In this process the temperature at which any reaction between molecular oxygen and aliphatic hydrocarbons begins is about 240 deg. C. Owing to the fact that the oxidation is slight at this temperature, and also to the further consideration that more heat is required to vaporize heavy hydrocarbons even with air, or air and steam present, higher temperatures than this must be employed. In general, the temperature should be as low as is consistent with good vaporization and a sufficiently rapid reaction; this varies, of course, with different petroleum fractions, but in any case no results of industrial value can be obtained above 500 deg. C. The writer's experience here would dictate that rather than work at temperatures approaching such a figure (where very high molecular weight hydrocarbons are being

treated) it is better to run a small amount of the heavy petroleum fraction—such as wax distillate, for example—with a large amount of a fraction of lower boiling range, such as gas oil or heavy kerosene, thereby effecting ready vaporization of the heavy portion and allowing a lower catalyst temperature for the reaction.

Although steam may be used with good results, too much steam hinders the reaction, so that with very heavy fractions it will not do to depend entirely on steam as an aid in vaporization.

Some Products of the Oxidation

The products formed vary somewhat with the catalyst and the temperature employed, but in general represent all the stages of the oxidation of aliphatic hydrocarbons from alcohols to oxygenated acids, together with hydrocarbons and oxidized bodies resulting from secondary reactions. These various bodies have not been studied in detail, but the acidic portion has usually been separated, and the non-saponifiable portion, which we have chosen to call "congeneric oil," has been set to one side without any further treatment, except in a few instances, when it has been subjected to distillation. The acids are not true fatty acids, but are oxygenated acids, which are always aldehydic in character and respond to all the aldehyde reactions; and, in fact, their future industrial application may in some cases depend upon their aldehydic character. For example, if the saponification of the oxidation product of any petroleum fraction be carried out with caustic soda, so much resinification of these acids takes place that when the acids are liberated from the soaps by a mineral acid they appear as hard resin-like substances. In fact, it is not at all improbable that these resinified acids will find use as cheap varnish gum and paint film substitutes.

If the saponification be carried out with calcium hydroxide instead of caustic soda, insoluble lime soaps are obtained of good color, since this base has very slight resinifying action on the aldehyde acids. The problem of making soda soaps of good color from these acids must be solved, the writer believes, by first making the lime soaps, then the free acids, and finally carrying out the soda saponification under conditions which do not permit resinification to take place.

It is rather interesting to note that in the lime saponification it is very easy to make greases, the original components being lime soap, "congeneric oil," and water, and finally, if desired, only lime soap

and congeneric oil. In fact, there is always the problem of breaking up the grease, if it is desired to isolate the acids as noted above. It is believed that the best method for doing this is to remove the water by evaporation and then thin down the congeneric oil with one of the lighter petroleum fractions such as kerosene, filter off the lime soap, and finally wash with a still lighter fraction, such as gasoline.

Development of New Fuel

Another phase of this work is the possibility of developing a new fuel from the cheaper fractions of petroleum by carrying out the oxidation at higher temperatures. These oxidized bodies thermally decompose to form both hydrocarbons of lower carbon content and oxidized bodies of lower molecular weight. For example, with a fraction of Mexican fuel oil boiling from 300 to 360 deg. C. and running the oxidation process (by the three-screen method to be discussed later) so that the temperature is held between 380 and 400 deg. C., the liquid product obtained amounted to 80 per cent by volume of the oil treated. This product contained 30 per cent by volume of aldehydic fatty acids, 20 per cent by volume of other aldehydic bodies, and the remaining 50 per cent consisted of other oxidized bodies and hydrocarbons. The latter were mostly of lower molecular weight than those of the original mixture, because of thermal decomposition of the oxygenated bodies. On distillation, 65 per cent of the product boiled under 300 deg. C. and of this fraction 18.4 per cent boiled below 200 deg. C. The oxygenated bodies are distributed through the entire range of fractions obtained by fractionally distilling the product, with more of the acids in the heavier fractions, and oxygenated bodies that have undergone thermal decomposition in the lighter fractions, along with hydrocarbons that have also been formed by thermal decomposition of the primary oxidation products. The distribution of the combined oxygen is shown by the following analyses made on a product obtained by the oxidation of a "pressure still tar," the residue from the "cracking" stills of one of the pressure cracking processes:

	Per Cent
Combined oxygen in fraction above 300 deg. C.	4.1
Combined oxygen in fraction between 200 and 300 deg. C.	6.48
Combined oxygen in fraction under 200 deg. C.	12.32

This fraction under 300 deg. C. might be called "oxidized" kero-

sene, and its properties certainly justify work in the direction of having it utilized industrially as a fuel in internal combustion engines. It may be used in kerosene engines, or blended with gasoline for use in gasoline engines. Although it has a somewhat lower fuel value than ordinary kerosene, owing to its oxygenated character, it undergoes much better combustion in the internal combustion engine.

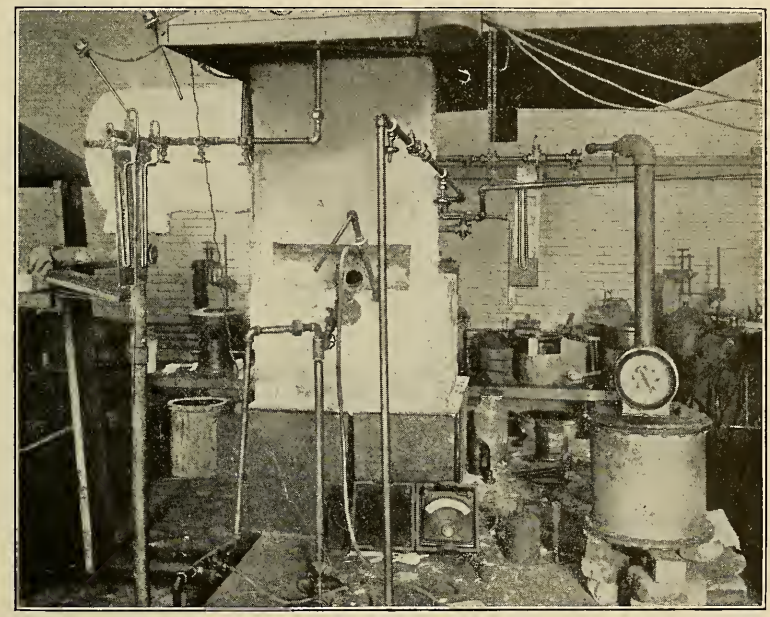

FIG. 1. Vaporizer (Right), Catalyst Chambers (Left)

A sample of "oxidized" kerosene made from Mexican gas oil, having a specific gravity at 15.5 deg. C. equal to 0.863, gave a calorific value of 18,210 B.t.u. per lb. A sample of Mexican kerosene that had been given a rather mild oxidation had a specific gravity at 15.5 deg. C. of 0.855 and gave a calorific value of 18,696 B.t.u. per lb. Three samples of ordinary kerosene from various sources gave for their calorific value in B.t.u. per lb. 19,827, 19,867, and 19,944, from which it would appear that the calorific value of these oxidized kerosenes is not seriously low.

The use of this oxidation mixture—such as is obtained from gas oil, for example—as a starting material in "cracking" processes has

been studied to some extent. As far as these experiments have been carried, it is evident that low boiling mixtures, within the gasoline range, can be obtained by the thermal decomposition of this mixture. These experiments are, however, only in the laboratory stage.

Heavier Fractions Possess Lubricating Properties

The oxidation products obtained from the heavier fractions deserve attention from the standpoint of lubricant manufacture. Southcombe has recently brought forward the idea that a small percentage of free fatty acids added to a straight mineral oil lubricant would increase the lubricating character, particularly for those cases in which it has been necessary to use "blended" mineral and fatty oils. While this has been questioned, the writer ventures the opinion that at the present time the experimental evidence collected supports Southcombe.

The portion of the oxidation mixture that will be found suitable for use, either alone as a lubricant or as a blending agent, is the "congeneric oil" remaining after the acids have been removed. These high molecular weight oxidation products have valuable lubricating properties, a fact which appears to extend the Southcombe idea in another direction.

Although the idea is a daring one, the writer has sufficient experimental evidence to make the claim that these oxidized oils will be found suitable for internal combustion engine lubrication. In this connection it should be remembered that the resinification property of these high molecular weight aldehydic bodies is brought out by treatment with the caustic alkalis. Under other conditions these bodies are really more stable than the fatty oils.

The sulphonation of the oxidation mixture has been carried out with a considerable degree of success. The acid portion sulphonates more readily than the other bodies present.

A promising application of the oxidation mixture in its entirety, just as it comes from the apparatus, is in the field of oil flotation. This mixture can serve primarily as a "frothing" oil in flotation mixtures, and numerous laboratory experiments have shown that it has, on the average, about one-half the frothing power of the best pine oil frother—that is, 2 gal. of this oxidized mixture will in general do the work of 1 gal. of the highest grade pine oil. When it is considered that this oxidized mixture can be made from fuel oil, available

almost everywhere, and that pine oil f.o.b. New York costs $1.50 per gal., it would appear that this product may find use in the concentration of ores by oil flotation.

From experimental evidence it is the acid content of the oxidized mixture that gives this material its frothing character. However, for flotation work there would be no gain in separating the acids, as the congeneric substances dissolve readily in all oil mixtures. The frothing oil in flotation formulas is but a small percentage of the total oil, hence the congeneric oils do no harm, and being made from fuel oil, which is commonly used as a collecting oil, the whole proposition works out as a very economical means of getting fatty acids into flotation mixtures.

Developing the Apparatus

This process has been carried to what might be called the semi-industrial stage. In the laboratory of industrial chemistry at the Carnegie Institute of Technology there was set up a triple screen apparatus large enough to make about a barrel per day of the oxidized mixture from any petroleum fraction or blend that can be vaporized.

When the larger apparatus was first installed, one screen only of catalytic material was used, and the excess heat developed was carried off by a system of cooling pipes, the closed ends of which were imbedded in the catalyst.

Either air or water could be used as the cooling medium. In this oxidation of aliphatic hydrocarbons the writer usually prefers to keep the temperature of the catalyst below 400 deg. C. (usually 280–380 deg. C.), hence in an apparatus larger than that used in the laboratory the temperature tends to rise because of the greater distance to any radiating surface and the non-conducting character of the catalyst and its carrier, which is usually asbestos.

The cooling tube apparatus worked fairly well, but later the double- and finally the triple-screen apparatus were developed. In the cooling tube system one catalytic screen only was used, hence all the air that was to be introduced had to be given to the reaction at one time. With more than one catalytic screen, the air is introduced in portions before entering each screen, being distributed among the screens usually in equal amounts, but sometimes varying from this, if conditions demand it.

The triple-screen system also makes possible the use of different

catalysts. It has been found that uranium oxide catalyzes the oxidation to the aldehyde stage, and at present uranium oxide is used for screen 1 and the molybdenum oxide mixture for screens 2 and 3.

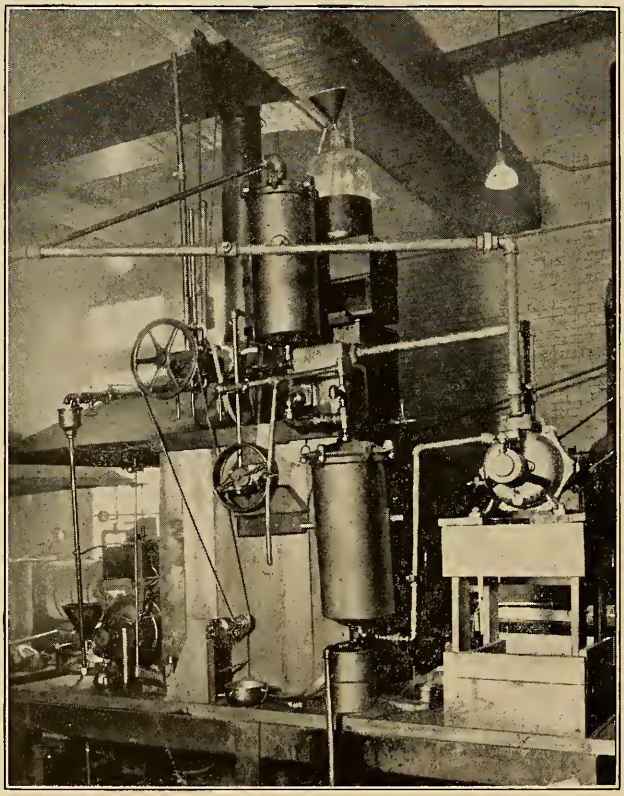

Fig. 2. Oil Feed and Exhaust Pump

The air is drawn into the system by a small pump, which, in addition, functions as a mechanical scrubber in aiding in the removal of the oil vapors from the gas stream. A parallel tube condenser placed about 15 ft. beyond the catalyzer (to allow for air cooling) is placed between the catalyzer and the pump.

Some Operating Data

The following example will serve to show the working of the apparatus:

Catalysts: three screens, all of molybdenum oxides, each 37.5 cm. in diameter and 1 cm. thick.

Oil used: Pennsylvania petroleum; a product sold at one time during the war as fuel oil by one of the Pittsburgh refineries: it showed the following on distillation:

First drop, 200 deg. C.	Per Cent by Vol.
200–250 deg. C.	11
250–300 deg. C.	51
300–350 deg. C.	34
Residue above 350 deg. C. and loss	4

Specific gravity of oil at 15.6 deg. C. was 0.819. Olefinic hydrocarbons (by the sulphuric acid test) was 7.5 per cent.

Time of run, 4 hours.

Average temperature of mixture leaving vaporizer, 310 deg. C.

Average temperature of first catalyst 335 deg. C.

Average temperature of second catalyst 370 deg. C.

Average temperature of third catalyst 370 deg. C.

Volume of air at room temperature and pressure passing into vaporizer and on into first catalyst, 70 liters per minute.

Volume of air added at second catalyst, 30 liters per minute.

Volume of air added before entering third catalyst, 30 liters per minute.

For the second half of the run, "fume" gas (50 liters per minute) was taken from exit line and added as diluent to lower the temperature at screen number two.

Rate of oil feed to vaporizer, approximately 6 liters per hour.

Rate of water feed to vaporizer, approximately 6 liters per hour.

Vacuum on system at vaporizer, 5 cm. of mercury.

Gas Analysis:

	Per Cent by Vol.
CO_2	2.9
O_2	2.9
C_nH_{2n}	2.5
CO	4.8
Undetermined (mostly N_2)	86.9

Volume of oil fed during run, 25.5 liters.

Volume of oily product (insoluble in water) recovered, 19.6 liters.

Specific gravity of product at 15.6 deg. C. was 0.86.

The product had approximately the following composition:

	Per Cent.
Aldehydic fatty acids	31
Aldehydes (above 200 deg. C.)	20
Alcohols, volatile aldehydes, and other oxidized bodies with hydrocarbons (by diff.)	49

The process works even better on oils having a lower market value than the Pennsylvania petroleum. For example, one of the easiest

fractions to treat is what is commonly called "the gas oil fraction" from Mexican petroleum. The presence of sulphur compounds and of unsaturated hydrocarbons is no drawback to the application of the process, since the oils containing these bodies oxidize more readily. This, therefore, makes the process applicable to many refining wastes that now find their way into the fuel oil tank.

Patent applications covering the main process as well as its various ramifications have been filed in the United States and foreign countries.

CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PA.

DISCUSSION

PRESIDENT WESSON: The paper is open for discussion.

DR. BROOKS: I would like to ask Professor James if he has ever run any of these stinking high sulphur oils and shale oil, and whether he can handle them in any way?

DR. JAMES: We have run them in the laboratory and had some trouble, but in general I prefer a sulphur oil, because it will oxidize more rapidly.

DR. BROOKS: I refer chiefly to the high sulphur shale oil, rather than shale.

DR. JAMES: Do you mean from Colorado?

DR. BROOKS: No; the English oils.

DR. JAMES: I have only used the Colorado shale oil, from which I have had a lot of trouble.

DR. MOORE: I would like to ask, if I understood correctly, whether there was not a mistake. Do you mean 5 inches of vacuum or 5 inches of pressure?

DR. JAMES: 5 centimeters.

DR. MOORE: 5 centimeters?

DR. JAMES: It was not a straight vacuum, but under slight suction, just to pull in the air.

A MEMBER: These sharp odors in these light products—can you cut them out?

DR. JAMES: I don't know whether that can be done. In the first samples which I sent to the West they said if you put that stuff in the mill it would drive all the people out of the mill. By blowing air

through it for two hours you can remove all that odor, and on the second sample sent we had no kick at all about it.

PRESIDENT WESSON: Has anybody any question? [No response.] There is one very interesting point comes up in this oxidization of fatty acids. I don't know about petroleum, but I have never yet seen an oxidized fatty acid that would make a decent soap and I don't expect to.

SOME ENGINE EXPERIMENTS WITH OXIDIZED OILS

By J. H. JAMES and F. C. ZIESENHEIM

Read at the Richmond Meeting, December 8, 1922

The writer pointed out in a paper read at the Baltimore meeting of this Institute last December that in the catalytic oxidation of petroleum hydrocarbons there is always a portion of the product having a lower boiling range than that of the raw material, and for convenience this was called "oxidized kerosene." As shown by the distillations of the oxidation products used in these experiments, this material always had between twenty and thirty-five per cent boiling under 200° C., while the upper limit in every case was taken at 300° C.

Further, it was noted in the paper referred to that the fuel value of these products runs about one-eighth below that of ordinary petroleum hydrocarbon mixtures boiling within the same range.

Reasoning from the work of other investigators, particularly that which had been done on alcohol, it was believed that these "oxidized kerosenes" might show desirable properties when used as a fuel in an internal combustion engine. To test out this idea, the experimental runs described below were made, particular attention being paid to the behavior of the engine as to any "knocking" or detonating characteristics of the fuels, as well as to the power developed in each case.

The fuels tested were: (1) ordinary kerosene (for comparison); (2) "oxidized kerosene" made by the oxidation treatment of Pennsylvania kerosene and taking the portion boiling up to 300° C.; (3) "oxidized kerosene" made in the same way from high sulphur Mexican kerosene; (4) "oxidized kerosene" made by applying the oxidation treatment to Mexican gas oil and distilling out the portion boiling up to 300° C.

The Engler distillations of the fuels used in the kerosene engine tests and in the later automobile tests are given below:

PENNSYLVANIA KEROSENE

Sp.gr. at 15.6° C. .800

Initial	193° C.	
Up to	200°	3%
Up to	225°	24%
Up to	250°	58%
Up to	275°	84%
Up to dry point	(300°)	96%
Distillation loss, etc		4%

OXIDATION PRODUCT FROM PENNA. KEROSENE (UP TO 300° C.)

Sp.gr. at 15.6° C. .847

Initial	112° C.	
Up to	125°	3%
Up to	150°	11%
Up to	175°	21%
Up to	200°	34%
Up to	225°	43%
Up to	250°	56%
Up to	275°	76%
Up to dry point	(300°)	96%
Distillation loss, etc		4%
Organic acids (not removed for test)		11%

OXIDATION PRODUCT FROM HIGH SULPHUR MEXICAN KEROSENE

Sp.gr. at 15.6° C. .8515

Initial	110° C.	
Up to	125°	2%
Up to	150°	5%
Up to	175°	11%
Up to	200°	23%
Up to	225°	44%
Up to	250°	68%
Up to	275°	86%
Up to dry point	(300°)	98%
Distillation loss, etc.		2%
Organic acids (not removed for test)		9.2%

OXIDATION PRODUCT (UP TO 300° C.) FROM MEXICAN GAS OIL

Sp.gr. of original oxidation mixture at 15.6° C. = .903
Organic acids in original oxidation mixture = 20%

Distillation on original oxidation gave:

Initial	110° C.	
Up to	125°	2%
Up to	150°	6%
Up to	175°	10%
Up to	200°	17%
Up to	225°	20%
Up to	250°	28%
Up to	275°	40%
Up to	300°	60%
Up to	325°	76%
Up to	350°	90%
Residue plus distillation loss =		10%

A distillation of this product was made, cutting out the portion below 300° C. for the engine test.

MOTOR FUEL No. I

Initial	72° C.	
Up to	105°	6.5%
Up to	125°	25. %
Up to	140°	43. %
Up to	150°	54. %
Up to	175°	80. %
Up to	190°	91. %
Up to	200°	94. %
End point	218°	98. % recovered.

The specific gravity of the sample was .798 at 15.6° C. and the acid content was 15 per cent., no refining whatever being carried out.

MOTOR FUEL No. II

Initial	82° C.	
Up to	105°	2%
Up to	125°	8%
Up to	140°	19%
Up to	150°	23%
Up to	175°	45%
Up to	190°	60%
Up to	200°	70%
Up to	210°	80%
Up to	220°	90%
Up to	235°	95%
End point	253°	99% recovered.

The material was refined to the extent of removing all the organic acids, the finished material showing a specific gravity of .798 at 15.6° C.

The kerosene engine used in the first set of experiments noted below was a one-cylinder, 10 h.p., 375 r.p.m., Mogul No. H 507, made by the International Harvester Co., of Chicago, and kept in somewhat intermittent use for instructional purposes in the Automotive Laboratory of the Carnegie Institute of Technology. This engine is provided with attachments for "warming up" on gasoline, and has forced feed lubrication. The water injection for lessening the detonation usual with kerosene engines is provided, and the readings of this adjustment bring out an important characteristic of the "oxidized kerosenes."

The following logs give the more important readings taken; in every case the engine was warmed up by running on gasoline.

Ordinary Commercial Kerosene (Penna. Petroleum)

I A

Reading No.	Time	R.P.M.	Brake H. P.	Fuel wts. lbs.	Fuel used between readings	Fuel used per B.H.P. hr.	Temperatures (Degrees C.)				Fuel Adj.	Water Adj.	Remarks
							Cooling Water		Air Heater	Exhaust			
							In	Out					
	P. M.												
1	4:35	394	9.17	17.344	..	..	55	64	60	425	4	8	These readings made as a trial in getting all adjustments. Preliminary trials without water injection showed extremely bad detonation.
2	4:45	392	9.17	15.750	1.594	1.043	58	69	60	423	4	8	
		Av. 393											

I B

3	4:58	392	..	13.906	..	..	65	75	54	480	4	11	This run determined the maximum water injection the engine would stand and carry the load. The detonation was still marked.
4	5:08	392	9.14	12.688	1.218	.799	65	75	55	470	4	11	
5	5:18	391	9.13	11.000	1.688	1.110	65	77	57	490	4	11	
6	5:28	396	9.17	9.375	1.625	1.063	66	79	57	490	4	11	
7	5:38	391	9.17	8.000	1.375	.900	67	78	57	495	4	11	
	40 Min.	Av. 392.4	Av. 9.15	Used 5.906	Total 5.906	Av. .968							

Oxidation Product from Penna. Kerosene (Up to 300° C)

2 A

8	A. M. 11:35	397	..	25.875	..	..	57	69	52	460	4	0.0	Readings 8 and 9, detonation noticeable, but not so pronounced as with no water trials with ordinary kerosene.
9	11:50	..	6.33	..	..	..	64	81	60	470	4	0.0	
10	11:53	403	6.38	..	..	..	65	81	63	480	4	4.0	
11	P. M. 12:01	403	6.39	..	..	..	65	78	64	450	4.3	4.0	Readings 10 and 11, detonation was practically silenced by this water adjustment.
12	12:11	395	6.33	..	..	..	65	79.5	63	470	2.3	0.0	
13	12:21	394	6.26	..	..	..	67	82	66	475	2.4	0.0	
14	12:25	..	..	19.938	5.937	1.125	..	..	..	..	..	..	
	Run 50 min.	Av. 398.4	Av. 6.35										

2 B

Reading No.	Time	R.P.M.	Brake H. P.	Fuel wts. lbs.	Fuel used between readings	Fuel used per B. H. P. hr.	Temperatures (Degrees C.) Cooling Water In	Cooling Water Out	Air Heater	Exhaust	Fuel Adj.	Water Adj	Remarks
15	P. M. 2:45	395	9.25	16.750	..	..	49.5	64.0	61	..	3.5	8	This water adjustment practically eliminated detonation.
16	2:55	398	9.25	15.375	1.375	.892	58.5	68.0	62	..	3.5	8	
17	3:05	393	9.22	14.063	1.312	.853	62.0	72.0	63	540	3.5	8	
18	3:15	397	9.21	12.563	1.500	.977	64.0	74.5	64	530	3.5	8	
19	3:25	390	9.17	11.188	1.375	.900	65.0	77.0	59	520	3.5	8	
	Run 40 Min.	Av. 394.6	Av. 9.21	Used 5.562	Total 5.562	Av. .906							

2 C

20	3:44	381	..	17.750	..	..	71.0	90.0	58	520	3.5	0.0	No water injection. Some detonation. Lower horse power and higher fuel consumption.
21	3:54	379	7.98	16.125	1.625	1.22	73.5	97.0	59	520	3.5	0.0	
22	4:04	..	..	14.313	1.812	..	69.0	91.0	59	495	3.5	0.0	
	Run 20 Min.	Av. 380		Used 3.437	Total 3.437								

Oxidation Product from High Sulphur Mexican Kerosene (Up to 300° C)

3 A

23	2:00	398	8.68	20.625	..	..	54	75	47.5	485	3.3	5	Exhaust clear. Lean fuel setting. Water injection sufficient to quiet detonation to "bomp, bomp" condition. Spark at full advance. Amount of water used for injection 3.35 liters.
24	2:10	398	8.68	19.500	1.125	.778	58	75	52.5	497	3.3	5	
25	2:20	398	8.67	18.313	1.187	.82	61	82	54.0	500	3.3	5	
26	2:30	397	8.67	16.718	1.595	1.103	63	84	56.0	505	3.3	5	
27	2:40	398	8.68	15.500	1.228	.843	64	86	57.0	502	3.3	5	
28	2:50	398	8.68	14.125	1.375	.951	64	90	57.5	500	3.3	5	
29	3:00	..	..	12.813	1.312	..	64	85	58.0	500	3.3	5	
	Run 60 Min.	Av. 397.3	Av. 8.68	Used 7.812	Total 7.812	Av. .899							

3 B

Reading No.	Time	R.P.M.	Brake H. P.	Fuel wts. lbs.	Fuel used between readings	Fuel used per B. H. P. hr.	Temperatures (Degrees C.)				Fuel Adj.	Water Adj.	Remarks
							Cooling Water		Air Heater	Exhaust			
							In	Out					
30	3:11	388	..	10.938	..	..	64	83	56.0	490	3.5	10	Trial for maximum load with this fuel. Exhaust had slight blue haze, odor not noticeable. Water injection as set *entirely quieted detonation*. Throttle nearly wide open as set by governor with speed below normal.
31	3:21	386	12.12	9.063	1.875	.928	63	80	56.0	480	3.5	10	
32	3:31	372	11.88	7.250	1.813	.916	62	80	56.0	480	3.5	10	
33	3:41	..	..	5.250	2.00	..	60	77	53.0	450	3.5	10	
	Run 30 Min.	Av. 382	Av. 12.00	Used 5.688	Total 5.688	Av. .922							

3 C

34	3:50	398	..	10.250	..	..	59.0	75	56.0	485	3.4	6.5	Half load test on this fuel. Water injection was set at quiet running, but some "bomp, bomp" was noticeable. Exhaust had slight haze at first, but became clear.
35	4:00	400	6.79	9.25	.938	.829	60.5	74	57.0	465	3.5	6.0	
36	4:10	400	6.81	8.125	1.15	1.10	58.0	80	58.0	480	3.5	6.0	
37	4:20	..	..	..	1.00	..	60.0	83	57.0	480	3.5	6.0	
	Run 30 Min.	Av. 399	Av. 6.80	Used 3.188	Total 3.188	Av. .965							

Oxidized Kerosene Made from Mexican Gas Oil

4 A

Reading No.	Time	R.P.M.	Brake H. P.	Fuel wts. lbs.	Fuel used between readings	Fuel used per B. H. P. hr.	Temperatures (Degrees C.) Cooling Water In	Cooling Water Out	Air Heater	Exhaust	Fuel Adj.	Water Adj.	Remarks
	A. M.												
38	11:00	394	..	14.188	..	..	60	73	43.0	440	5.0	5.5	Water injection sufficient to bring detonation down to the "bomp, bomp" condition. Would take no more water and hold load. Exhaust showed considerable smoke with a very pungent odor. This is the leanest mixture engine would run on for this load.
39	11:10	398	8.64	12.500	1.688	..	61	76	45.5	445	5.0	5.5	
40	11:20	400	8.71	10.563	1.937	1.172	62	77	44.0	450	4.0	5.5	
41	11:30	398	8.71	9.500	1.063	1.335	62	80	48.0	490	4.0	5.5	
42	11:40	397	8.67	8.063	1.437	.733	62	78	45.0	440	5.0	5.5	
43	11:50	394	8.63	6.625	1.438	.995	62	80	47.5	450	5.0	5.5	
44	12:00	..	..	5.000	1.625	1.000	62	83	44.0	..	5.0	5.5	
	Run 60 Min.	Av. 396	Av. 8.67	Used 9.188	Total 9.188	Av. 1.047							

4 B

45	4:30	400	..	10.250	..	..	61	85	54.0	480	3.5	5	Lighter load than 4a test. Exhaust clear. Engine ran evenly. "Bomping" noticeable but not objectionable. Injection water used .73 liters.
46	4:40	402	6.82	9.250	1.000	.88	62	80	57.5	500	4.0	5	
47	4:50	..	..	8.125	1.125	..	62	84	60.5	500	4.0	5	
	Run 20 Min.	Av. 401	6.82	Used 2.125	Total 2.125	.88							

Additional experiments bearing on the same line were tried as follows on the two oxidized fuels within the gasoline range:

The motor fuel No. I was tested in a six-cylinder car (28 h.p.) which was run for 90 miles under all sorts of city traffic conditions, yielding 20 miles per gallon, under the same conditions which gave with ordinary "58–60" gasoline 14 to 15 miles per gallon. The most marked feature of the test was the freedom from detonation with spark advanced and on hills, where the "58–60" fuel gave persistent knocking.

The No. II fuel was used in a touring test in the same car with the following results:

Lighter gasoline was needed for priming the cold engine. The road touring test consumed 10.8 gallons of fuel, giving an average of 16.5 miles per gallon. With spark advanced almost no detonation was observed at any stage of the run. Similar tests with "58–60" gasoline gave about the same mileage, but noticeable detonation.

Realizing that part of the foregoing results on the oxidized kerosenes were obtained because of the presence of the fraction boiling below 200° C., it should be pointed out that this portion does not have the ordinary gasoline distillation curve by any means; hence, if we call the portion from 200° to 300° C. kerosene, the under 200° portion resembles, as far as its distillation goes, a heavy naptha. Looked at in this light, these oxidized fuels up to 300° C. might be regarded as mixtures of ordinary kerosene with heavy naptha, in ratios from 4:1 to 2:1.

As bearing on this point, an engine run was made with the oxidized Mexican kerosene in the automotive laboratory of one of the large oil companies. The behavior of this fuel as to detonation was checked against a kerosene-gasoline mixture that would give the same low detonation characteristics. It was found that a mixture of 60 per cent kerosene and 40 per cent gasoline was required to bring ordinary kerosene down to that of the oxidized kerosene in low detonating character.

When we note that all the oxidized fuels tried in the kerosene engine have one-eighth lower thermal values than ordinary hydrocarbons within the same distillation range, and still gave as good efficiencies as, or better than, ordinary kerosene, the writer believes that we must look to the chemical character of the mixtures for the expla-

nation. According to this idea the original hydrocarbon molecules are weakened toward the oxidation attack in the internal combustion engine because of their oxidized character, so that a better "clean up" results, and perhaps more of a propulsive effect during the explosion which is evidenced by a diminution of the detonation.

Summary

Engine experiments with a fuel made by the catalytic oxidation of kerosene and a fuel of similar character made by the oxidation of gas oil have been described.

The oxidized kerosenes show approximately the same power development as ordinary kerosene, in spite of the fact that their thermal value is one-eighth less. It is believed that there is a better "clean up" in the combustion of these partially oxidized fuels, which accounts for their efficiency.

These oxidized kerosenes show lower detonation tendencies than the straight hydrocarbon fuel.

Similar experiments with lower boiling oxidized fuels in an automobile engine gave results which show that the above results hold here as well.

Carnegie Institute of Technology,
Pittsburgh, Pa.,
November 29, 1922

Discussion

Mr. Huff: I should like to ask Professor James if he has noticed any gum formation in the use of this fuel. I understand that gum formation is a very fundamental question in the use of fuels in internal combustion engines. An investigation by the Bureau of Mines goes to show that oxidized gasoline gives a heavy yield of gums I presume that has been considered, and I should be glad to know more about it.

Mr. James: I might say that most of the gum is in the fraction over 300° C. As bearing on the gum formation problem, we took the oxidation product fractions over 300° C. and made a lubricating oil from them by careful vacuum distillation. In this same kerosene engine there was no varnish-like formation with this lubricant, and the carbon formed was only about half that formed from well-known

commercial engine oil lubricants. This carbon was of a light, fluffy character. I believe that here again the chemical character of the oil is the determining factor in the cleaner combustion.

PRESIDENT HOWARD: I should like to ask Professor James if he used water injection in these practical tests in an automobile?

MR. JAMES: No; they were run in the usual way. No water injection whatever.

VAPOR TENSION AT LOW TEMPERATURES

By N. T. BACON

Read at the Niagara Falls Meeting, June 21, 1922

Willard Gibbs, and his school of physico-chemists, a generation ago warned against trying to apply to individual molecules the mathematical formulas which they worked out to represent conditions of the averages of great numbers. Unfortunately these scholars made no attempt to set a limit below which these formulas could not be held to apply and, therefore, this warning has been lost sight of until we find Nernst and his followers pushing their ideas of what are logical mathematical deductions into what must be looked upon askance, even at the best, because in their processes of reasoning they constantly overlooked the ordinary necessities of the case. Of course, there must be mathematical laws governing the case of the individual molecule, but we should proceed with much caution in developing these.

The interpretations put by Dr. Langmuir on the extremely beautiful experiments which he has made on the highest kind of vacuum seem to me to be open to this criticism. He has measured down to limits, below which it seems improbable that any vapor of the substance can exist, a continuously varying function which he considers to be the probability of a molecule of the substance existing as a vapor in his apparatus. Because he can follow this function to extremes where it becomes infinitesimal, he feels assured that vapor tensions exist for all substances at even the lowest temperatures attainable, although by his calculations at the temperature of liquid air a sphere of six times the diameter of the earth would be necessary to accommodate a single molecule of platinum. Probably a molecule of carbon would require many times this space and he has calculated that the solar system would not accommodate one of tungsten.

It seems to me that we need to get back to consideration of the mutual relations of the different phases of substances, bearing closely in mind the characteristics of each phase and the method by which such characteristics can be maintained. I believe that a clear view

of what is involved by this assumption of ultimate tenuity will go far toward disproving this hypothesis.

Probably no one will object to the following statement of characteristics of a saturated vapor:

I. It must always make equal pressures in all three dimensions.

II. To insure saturation, it must be in contact with a surface of the same substance in either solid or liquid phase, except as under certain conditions we can have the vapor in equilibrium with some such combination of the same as a hydrated crystal instead of the substance itself, or with a solution of the substance.

III. It seems to me a necessary corollary of our ordinary doctrines that the condition of each molecule in the condition of saturated vapor is affected not only by the liquid or solid phase present, but also by other molecules of the same also present in the vapor condition.

IV. The vapor tension is much influenced also by the physical structure of the solid or liquid phase. It is thoroughly recognized that vapor tension is higher from a mist of water particles of infinitesimal diameter than from a flat surface.

V. For any ordinary length of experiment, and even in some cases permanently, the vapor tension is also affected by the nature of the walls of the containing vessel, even though this be of a substance with which the vapor forms no chemical combination.

VI. The vapor tension is likewise affected by the presence therein of certain foreign substances with which again the vapor forms no chemical combination.

VII. These differences due to foreign substances appear to be much more important at low temperatures than at high.

VIII. The effect on the vapor of the substances in V and VI varies greatly with the physical structure of these substances, being apparently increased by a multitude of infinitesimal forces.

According to our present definitions, in order to determine the saturation pressure of any vapor, there must be a surface of another phase of the same substance exposed to contact with the vapor, otherwise vapor tensions can be obtained much exceeding that of true saturation. In such a case, therefore, as that of platinum at 75° C. absolute temperature, which is about the temperature of liquid air, where a single molecule of platinum requires many times the volume of the earth to give it elbow room, what reason is there to expect that a molecule of platinum, which happened to be hovering over the south

pole, would be affected by the nearest exposed surface of platinum, which probably would be at least 3,000 miles away and so situated that the curvature of the earth would intersect the straight line between the two? Could we, under these circumstances, expect the supposititious vapor molecule to be in any way governed by this? At this temperature, even supposing the molecule of platinum to be monatomic, its velocity would be only about 100 yards per second, which is about the speed of an aeroplane, and even if it made the shortest possible course for 3,000 miles and back, it could only make one contact in 24 hours with the platinum surface. Is it reasonable to suppose that such very infrequent contacts (unless we assume specific molecular attraction acting through immense distances) would be enough to affect the situation at all, especially as the chances are millions to one against the molecule making a straight line in either direction?

A few years ago I brought up the question of the method by which a single molecule of barium sulphate could exhaust the solvent power for barium sulphate of about ten million molecules of water. This is equivalent to having one molecule of barium sulphate at the center of a cube having approximately two hundred and seventeen molecules of water on each side, in which each molecule of water is affected to the same extent by a central molecule of barium sulphate, for otherwise the amount dissolved by the central molecules of water would be greater than that by the molecules relatively much farther away, so that these would not be saturated and, therefore, the mass of water would be able to take up more barium sulphate, so as to equalize conditions throughout the cube.

I was able to imagine an explanation of this on the hypothesis that the molecule of barium sulphate resolved itself into electrons circulating throughout the mass so as to furnish frequent contacts with the individual molecules of water, while such electrons were guided and controlled by the specific conditions characterizing their coexistence as barium sulphate. While this hypothesis may not satisfy others, it did enable me to present the facts of the case to myself so that I could get a mental picture of what might be happening, which was a great improvement on having no working hypothesis of any kind. But in the case of a vapor molecule no such explanation seems possible, for all our theories with reference to gases start on the assumption that the individual molecules act as units, and Dr. Langmuir's

work is based on this hypothesis. Unquestionably he measured some real function, but for my part it is impossible to believe that this was the probability of having in the apparatus a molecule in vapor condition of the substance under consideration. Is this function not much more likely to have been one of the amount of energy which must be supplied to one molecule under the given condition of temperature to bring it to the vapor condition?

In turning over in my mind the question of vapor tension, it would appear that in order to have the condition of a true vapor we must have present at least three molecules of the substance under consideration to satisfy the conditions of having at least one molecule in liquid or solid phase, as a determinant of its condition; and to furnish, likewise, the interrelations of molecules in the gaseous phase in the unit of space under consideration. This may be regarded as the differential of space, even though it far exceeds the ordinary conception of the size of a differential. This, therefore, would seem to place a limit of two molecules to the differential of space as the lowest to which a true vapor pressure could be reduced. Very likely conditions could be brought about by which this space would contain but a single molecule. However, as I regard it, under these conditions, this molecule could not properly be reckoned to make a vapor pressure, although it might be moving with the same velocity as we should expect for such a gaseous molecule, but it would be merely a sporadic phenomenon. The conditions of other molecules in either liquid, solid or gaseous phase would not be affected by accidental elimination of this one from the system, if it could be accomplished without other change in the system, and we should have no method of determining whether such individual molecule were solid, liquid, or gaseous, so far as our present resources extend. Two molecules, therefore, to the differential of space would seem to be the lowest limit to which a vapor pressure can be reduced and still be reckoned as a vapor pressure from this point of view.

Approaching this question from another side, and assuming in a given space a single molecule, we shall see readily that if this happened to be moving in the direction of any one of the principal axes of a cube, this would act in one dimension. There is one particular angle of incidence at which this molecule could be so directed as to strike with equal force on each of the limiting faces of a cube, so as to produce equal pressure in all the three dimensions, but there is only

one chance divided by infinity squared of a single molecule attaining this direction, and the chance for equal pressures on the three dimensions is not much better with two; but when three molecules coexist in the same space it is easy to imagine that conditions might bring about equal pressures in all dimensions. Here, again, we have a probable lower limit to vapor pressure of the same order as, though not quite numerically equal to, the limit laid down above.

Langmuir and others have shown that apparently one gas after another suddenly seems to lose all vapor tension as the temperature approaches the absolute zero. Langmuir attributes this to adsorption of specific gases by the walls of his apparatus.

This is probably a correct enough explanation if we look upon it as being the result of reduction of the temperature to a point below which the substance in question can not continue to exist as a gas, as it must still be somewhere, and probably will be no longer in rapid motion. Light is thrown on this by the enormous adsorptive power of charcoal for almost all vapors, though this is to a certain amount selective. This, at low temperatures, becomes almost incredible, but I believe the explanation, after all, to be a simple one. The heat generated by this occlusion is greater than that due to liquefaction. There seems to be a ready explanation for it on the hypothesis that each individual gas has a limit below which that substance can not exist in gaseous form. This hypothesis is based on an assumption which Dr. Langmuir himself recognizes, namely, that of the imperfect elasticity of the molecule. According to this hypothesis, the gaseous molecules condensed by carbon are affected in the following manner: as they penetrate the pores of the carbon, owing to the imperfect elasticity of one substance or the other or both, part of the energy of translation of the gaseous molecule is converted into heat, with deformation of one or the other molecule by disarrangement of the electrons forming the molecule, and the heat thus generated is conducted away by the solid mass of the charcoal so that only a part of it is available to be transformed into kinetic energy, so that on the first contact there is considerable loss of velocity. Within the pores of the charcoal the molecule, thus having lost much of its initial velocity, speedily strikes again on another surface of the charcoal where again it loses velocity and so on, until finally it strikes on the surface at so low a speed that it does not rebound at all and is there adsorbed practically in solid condition instead of liquid, which

accounts for the very high heat of condensation. The great difference in condensing power of charcoal according to the method in which it is prepared, although chemically the same, shows that this is a physical characteristic instead of a chemical one.

I have made a diagram showing the curves of the pressure produced by 10^{20} molecules of various substances confined in the space of one cubic centimeter. Of course, with most of those under consideration, part will be in the liquid or solid condition and only a part volatile. For many of these there is a striking similarity; but, on the other hand, others intersect. The data are sufficient to be really interesting, however, only in a very limited number of cases, as the range of temperature and pressure over which most substances have been investigated carefully is very small. Almost nothing else, beside water and mercury, has been followed down to infinitesimal pressures and low temperatures, though some of the organic compounds, which volatilize only at relatively high temperatures, have been followed down to very low pressures. With many of these the only data available are those for vapor pressure, and, in order to obtain curves representing anything like these conditions, it has been necessary to follow these up by means of determinations of the vapor pressure, where more than this number of molecules were present. I believe that study along these lines will prove convincing to anyone who will make it for himself that there is a limit below which vapor tension does not exist because there can be only one or two sporadic molecules in the apparatus, and of these the phase can not be determined. I do not attempt to reproduce this diagram because it would cover such an enormous piece of paper if it is made on a large enough scale to show anything concerning such substances as helium and hydrogen and at the same time take in the data for phosphorus and sulphur, not to mention carbon and tungsten.

I am inclined to think that we shall find ultimately some simple relation between the critical point above which a substance can not exist in liquid phase and this lower critical point below which the same substance can not maintain a true vapor pressure. I can not place any faith in the possibility of an asymptotic curve of constantly declining pressure for a vapor of any substance like tungsten of which no vapor pressure is perceptible at any temperature which we are able to handle, or even with carbon of which we can just appreciate the vapor pressure at temperatures within our reach. The probability,

moreover, of the existence at infinitestimal temperatures of immensely complicated molecules like those of some organic compounds containing hundreds of atoms must be looked upon as very dubious on account of the extremely slow motion which these would have. At a temperature of some 50° C. absolute, the velocity of some of these heaviest molecules would hardly exceed thirty miles an hour, and with the great size of the molecule the probability of this becoming lodged and, therefore, absorbed in the pores of any more or less porous solid body with which it may come in contact is sufficient reason for thinking it unlikely to be able to maintain itself as a vapor; and as the temperature drops below this to that of liquid helium, the velocity would again be reduced to something like one-fourth of that at fifty centigrade absolute.

We may be obliged to make a new definition of vapor pressure to correspond with new data, but accurate definition is the most fundamental necessity of mathematical treatment, and this should be the first step before cutting loose from our present definitions.

PEACE DALE, R. I.,
February 1, 1922.

DISCUSSION

PRESIDENT HOWARD: This paper is open for discussion. Dr. Taylor.

DR. TAYLOR: I would like to make a few remarks on the measurements of one molecule. You can actually measure the heat changes in combinations of this kind, but no one can tell what the affinity of one molecule of ammonia is with one molecule of hydrochloric acid. There is no such thing. If you keep both in one vessel, you can not calculate what is the free energy involved nor when reaction will occur. In other words, all our chemical science at the present time is merely statistics. We elaborate statistics and we present facts in a statistical manner. I don't know where is the lowest limit at which the statistical method applies, but I have an idea that it is much lower than anything we have been able to get with anything like Langmuir's experiments in high vacua. We are told that there are more molecules in a tiny bulb of a flashlight than there are people on the face of the earth at the present time. In regard to the case of one molecule of barium sulphate in solution, I don't think we can consider it. What we have is the statistical relation of a large number of molecules passing into the medium of water, and the rate at which those

molecules are removed from the medium of water by adhering to solids. I personally can not subscribe to the view that vapor pressures will suddenly show a distinct drop beyond which vapor pressures can not be measured. I can not conceive of any such set of circumstances.

MR. BACON: Langmuir says that in one case mercury vapor goes down to a certain point and then ceases, which he ascribes to adsorption. Taking a case of that kind, the question was raised whether an equilibrium would not finally establish itself if given a period of time in order to establish a relation between the vapor and the liquid under all circumstances; whether there would not then finally be a vapor condition which would be a continuance of what had been hitherto. But there would come in a question of quantity. Assume 100,000 molecules in a flask, and that down to a given point the vapor pressure maintained itself as perhaps ten or twenty or say one hundred molecules in a vapor condition, and then it went out. Langmuir says this would be because of adsorption. The 100,000 molecules would not be enough to plate the entire surface of the thing, so that we would still have the reduction due to adsorption. The equilibrium would be between the adsorbed molecules and vapor molecules, so that there would never be a higher vapor pressure than the one due to the adsorbing vapor surface.

DR. WADSWORTH: I may have misunderstood Mr. Bacon on the mechanics of absorption, but it just occurred to me that if we assumed that mechanics are fixed and the adsorption of a given molecule, it would be somewhat difficult to explain the activation of charcoal on that basis, would it not, which has, I believe, somewhat the same special relation before and after activation and a very much greater adsorption value.

MR. BACON: Physical condition has much to do with the adsorbing power.

DR. TAYLOR: I do feel sure that one molecule here and there on the surface of copper are capable of holding a certain number of carbon monoxide. There is a statistical relation between the two.

MR. BACON: All adsorption seems to be more or less selective, and I should expect a priori that it would depend upon the construction of the molecule and one thing and another, and that one substance would be more apt to hold one substance than another, on account of the construction of the molecule, which would be quite irregular in shape.

Dr. Thatcher: I should like to inquire about the relation of incandescent lamps. The phosphorus is vaporized in a vacuum. It used to be thought that the process was adsorptive. However, in the litigation on the original patent our directors investigated adsorption and found that not only oxygen, but almost any gas, is adsorbed by carbon vapor. For example, carbon monoxide is not organic, which unites the particles or adsorbs to such an extent that immeasurably high vacuum is obtained. I think it is therefore a great question whether adsorption is chemical or physical. In that case it is no doubt physical.

VAPOR RECOMPRESSION SYSTEMS FOR EVAPORATORS

An Unprejudiced Survey of the Advantages and Shortcomings of Regenerative Evaporation—A Technical History of Its Development and an Analysis of Recorded Data on Test Runs.

By W. L. BADGER

Read at the Baltimore Meeting, December 9, 1921

Imagine a simple evaporating device, with liquid boiling in it at atmospheric pressure. Also assume that it is heated by steam at 10 lb. gage (240 deg. F.), that no heat is lost in heating feed, in radiation, or in any thick liquor drawn off, and that the condensate leaves at the temperature of the boiling liquid. To evaporate 1 lb. of water will take 970.4 B.t.u., and 1 lb. of steam will give up 980.4 B.t.u. A very slight change in our fundamental assumptions will make the two exactly equal. Then what is happening really comes down to converting 1 lb. of steam at 240 deg. and 10 lb. gage to 1 lb. of steam at 212 deg. and atmospheric pressure.

Now, if the hot condensed water is returned to the boiler without loss, we will have to add 980.4 B.t.u. to regenerate a pound of heating steam. But the pound of atmospheric vapor formed contains 970.4 B.t.u. more than the condensate. Why not, then, merely add 10 B.t.u. by compressing the steam instead of 980 to raise more steam? By this line of reasoning many times as much evaporation could be obtained per pound of coal burned than by raising steam direct, even after allowing for all kinds of losses.

Much has been written on this subject, but the articles have usually had a partisan bias. It is the purpose of this paper to give as nearly as possible an unprejudiced survey, and show the faults as well as the advantages of the system.

Historical and Descriptive

The first record of vapor recompression is a patent[1] by Pelletan in 1840 (36).[2] His apparatus is shown in Fig. 1. A pan *m* has a

[1] In (12) this date is given as 1834.

[2] Numbers in parentheses refer to bibliography at end of this article. Numbers below 100 are articles and above 100 are patents.

cover *T* supported by counterweights. Heating is done by two coils *g*. High-pressure steam is admitted by *E* and *F* to the injector nozzles *B*. These draw vapors from the pan through pipes *a* and compress them in the coils. This apparatus was unsuccessful, partly due to faulty nozzle design and partly to the very low boiler pressures then carried.

The Piccard-Weibel System

In 1874 Koerting (25) suggested the use of steam-jet nozzles for drawing non-condensed vapors from the steam spaces of evaporators, and mentioned that these vapors, together with the steam which operated the nozzle, would be compressed enough to be returned to the steam space (28). Nothing was done, however, till the advent of the Piccard-Weibel system in 1879 (30). It received considerable notice through the '80s (6, 11, 15, 26, 27, 40, 43, 44). Fig. 2 shows the system applied to a single effect evaporator. The reciprocating compressor *C* takes vapor from the dome *A* and compresses it to be used in the steam space. This figure shows how early it was realized that in such installations all possible heat must be saved, for the heat interchanger *S* is provided to heat the feed by the heat of the condensate. If the compressor *C* were to be steam driven, the exhaust was best utilized in a triple-effect as shown in Fig. 3.

This system was employed in several salt plants in France and Austria, and in a few sugar mills. It was installed in the mill at Pohrlitz in 1882. Weibel (43) reports that the mill, of 225 tons per 24 hours, sent about one-third of the juice to the thermocompressor evaporator. This was a triple of 150, 60, and 80 sq. m. respectively (vertical tubes). The compressor was 31.5 x 19.5 in. (fifty strokes per minute), took steam at 59 lb. gage, and exhausted at 6 lb. gage. It took vapor at atmospheric pressure from the first effect and compressed it to 6 lb. One lb. of boiler steam theoretically should have compressed 2.5 lb. vapor and furnished 1 lb. of exhaust, which would have evaporated 3 lb. in the triple effect, making a total of 5.5 lb. evaporated per pound steam. A very complete test was later made on this system (31, 42) which showed actually 4.4 lb. of water evaporated per pound of steam. While the Piccard-Weibel system was retained for a considerable time in salt works which had ample water power, it never gained a foothold in the sugar industry because of the excessive size and, at that time, rather poor design (11) of the reciprocating compressors needed.

The Nozzle Compressor

In the later developments, two lines of work have been followed—the nozzle compressor and the turbo-blower. Along the line of nozzle developments the principal place is held by Prache and Bouillon, who in 1905 developed a steam-jet nozzle (102), such as is shown in Fig. 4, and which was claimed to be far superior to any other. The nozzle alone can not make a practical device, and an explanation which anticipates the theory must therefore be introduced.

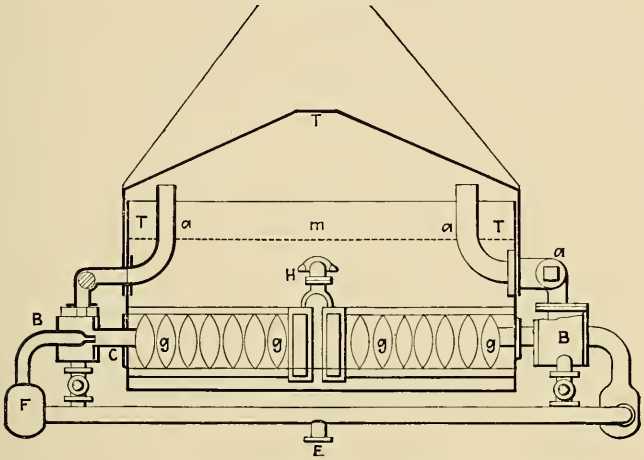

FIG. 1. Vapor Recompression Apparatus of Pelletan

In order to obtain a satisfactory capacity of the nozzle, the pressure range through which the vapor is compressed must be small. Neglecting minor factors, this pressure range is made up of two parts:

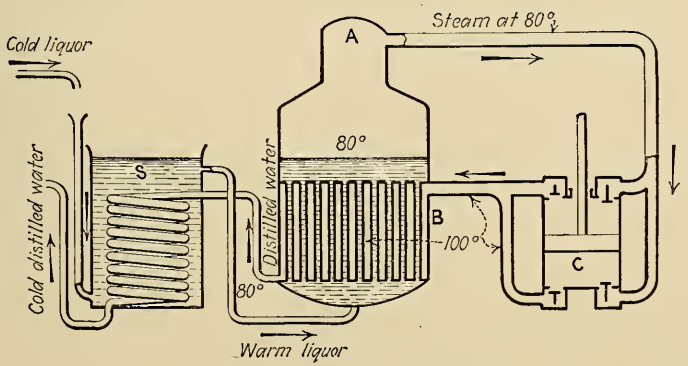

FIG. 2. Piccard-Weibel System

(*a*) the elevation in boiling point of the solution, (*b*) the working temperature drop. The first part can not be changed, but its effect may be minimized by confining the concentrated liquid to one part of the apparatus; for when an ordinary evaporator works continuously, the whole body is full of liquid at the final concentration. The second factor is, of course, within the control of the designer; but the smaller it becomes, the larger must the apparatus be for a given performance. If an evaporator could be designed with an unusually high coefficient of heat transmission, an evaporator for a given duty could operate on a smaller temperature drop than usual without increase in size. Hence the features to be noticed in the recent developments are (1) isolation of the more concentrated parts of the solution, and (2) attempts to increase the heat transmission coefficient.

Prache and Bouillon (or as later organized, La Société d'exploitation de procédés evaporatoires système Prache et Bouillon) first developed the evaporator shown in Fig. 5 (4, 5, 36, 101, 114, 123, 133). Here the liquor space of an ordinary vertical tube evaporator is divided by partitions, *P*, which extend some distance above the upper tube sheet and also completely divide the liquor space below the tube sheet. Each compartment has its own downtake *n*, and in the center of each downtake is a pipe *O* leading to the next compartment. Thus a part of the liquid is continually being passed from compartment to compartment, being finally withdrawn from 7. In this way the solution of highest boiling point is localized in the last compartment and only a part of the heating surface is handicapped by this loss in temperature drop.

The steam space is not divided. Therefore, if the vapors are compressed enough to give the desired working temperature drop for the dilute liquor, the compartments containing concentrated liquor will have a smaller temperature drop. But it is just these compartments which need a larger working drop than the others, because of the effect of their increased viscosity and density on heat transfer. If, on the other hand, the vapor is compressed sufficiently to give a satisfactory working temperature drop for the last compartment, it will result in a range of compression too great to be economical for the others.

A Horizontal Tube Evaporator

Prache and Bouillon later devised another evaporator which was to minimize the effect of boiling point and also increase the heat

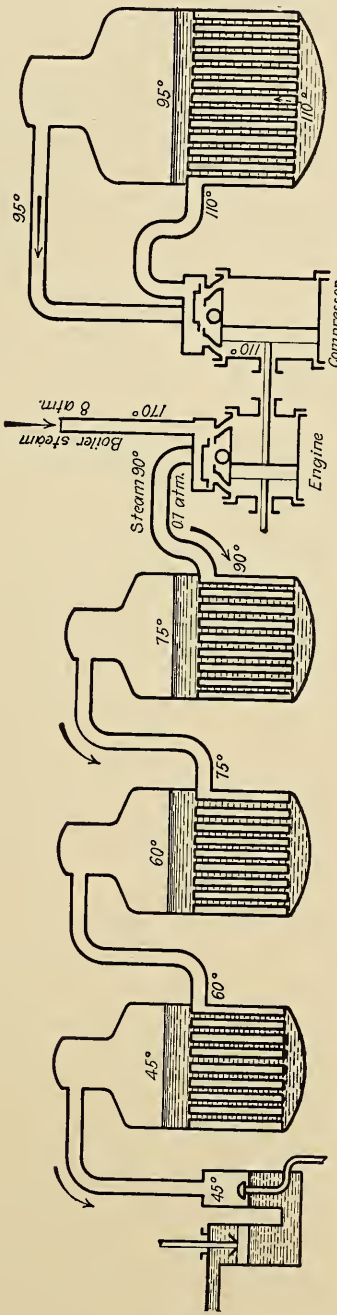

FIG. 3. Piccard-Weibel System Using Compressor Exhaust

transfer coefficient. Fig. 6 (4, 38, 134) shows this evaporator, consisting of several compartments side by side, each containing inclined tubes with liquor inside, and arranged in series as to liquor feed. All the compartments discharge into a common header, which is, however, provided with partitions to keep the liquor from each compartment separate from the others. A wide tube *E* for recirculation is provided at the bottom, and means (not shown) are also provided for transferring the liquid from compartment to compartment. Cold feed from *A* first passes through the preheater *B*, then by pipe *C* to

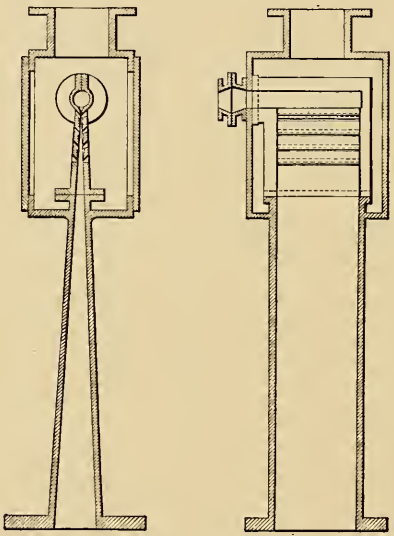

Fig. 4. Prache and Bouillon Nozzle

the evaporator, circulating through each compartment and finally leaving at *F*. Vapors from all the compartments collect in *I*, are compressed by boiler steam in the nozzle *H*, and go from compartment to compartment in pipes *K*. Here evidently the amount of compression for all the vapors is sufficient to overcome the elevation in boiling point in the last compartment.

Since the compression is done by a steam jet, there is a continual supply of steam to the apparatus above that which can be condensed by evaporation. Hence there is a pipe from the steam chamber *I* to the preheater *B*, and from there to an exhaust or to a condenser. The apparatus works in single effect; the compartments differ only in

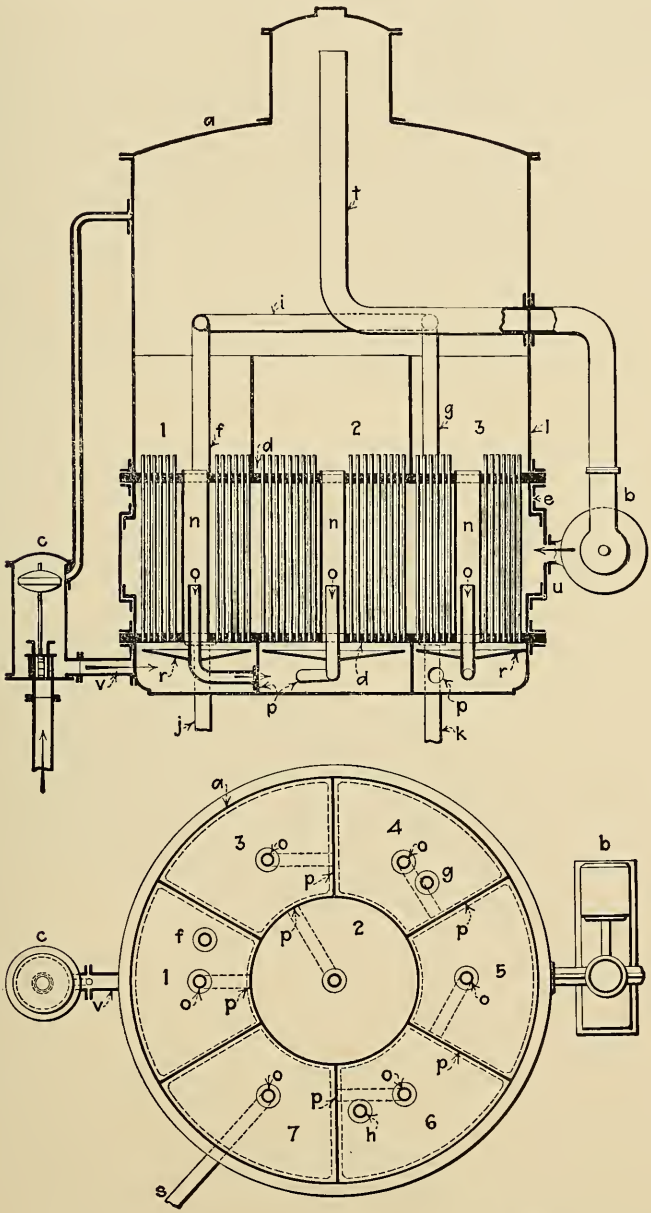

FIG. 5. Prache and Bouillon Vertical Tube Evaporator

the concentration of the liquid in them, and there will be little drop in pressure along the pipes *K* leading steam from compartment to compartment. The statement is made (4) that the heat transmission coefficients obtained in this evaporator are about double those of an ordinary evaporator. The same writer states that at that time (1916) about seventy-five Prache and Bouillon plants were in operation.

A similar evaporator patented by these workers has the compartments superimposed in one common shell. Fig. 7 (104, 117, 139, 144).

Recently a nozzle as applied to evaporators has been developed by de Baufre at Annapolis (13, 39, 107, 109, 110, 111, 145), and is shown in Fig. 8. In ordinary operation, high pressure steam is ex-

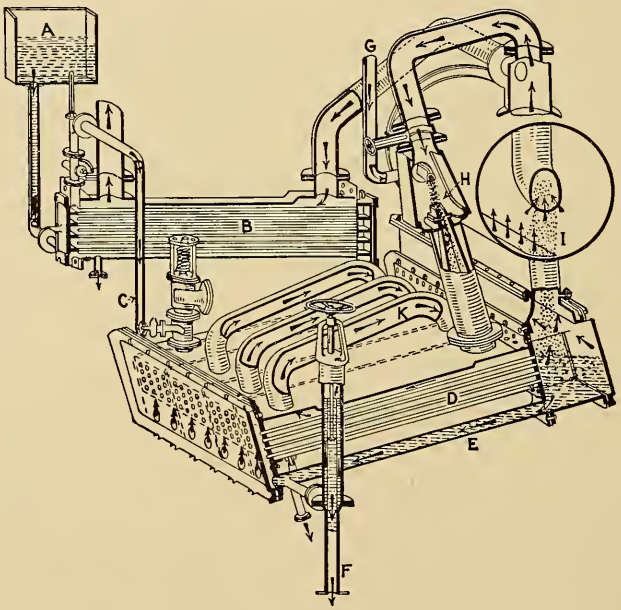

FIG. 6. Prache and Bouillon Horizontal Tube Evaporator

panded through the orifice *B* and nozzle tube *C*. Vapor from the evaporator is drawn in through the inlet, and the mixture of compressed vapor and expanded high-pressure steam is discharged through *K* to the evaporator coils.

Nozzle Performance and Design

The performance of nozzles has been studied and some results reported. Eslancher (17) has reported data on the Prache and Bouillon nozzle which have been copied several times (55, 38). From these data Fig. 9 has been drawn. This shows the ratio of (pounds vapor) to (pounds high-pressure steam) for different steam pressures, vapor temperatures, and temperature drops. By temperature drop is here meant the difference between the temperature of the steam in the heating space and the temperature of the boiling liquid. It will be noticed that the capacity of a nozzle falls off rapidly as the working temperature drop increases and as the pressure range through which the high-pressure steam is expanded decreases. It is obvious why the working temperature drop for such systems must be held below 10 deg. C.

De Baufre's nozzle has also been tested (13, 39). The data are represented in Fig. 10. The curve for nozzle tip No. 2 is reproduced as Curve 2 in Fig. 11. Curve 1, Fig. 11, is obtained from Fig. 9 for 175 lb. steam (the conditions under which de Baufre's nozzle is

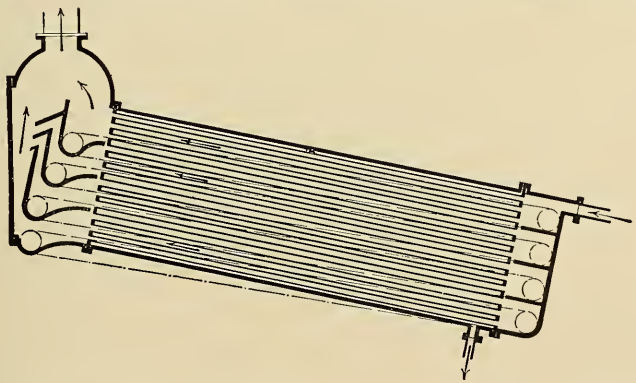

Fig. 7. Prache and Bouillon Evaporator with Superimposed Compartments

tested). There have been a number of patents involving the use of nozzles about which there is little or no information available (112, 120, 121, 125, 131, 138, 147, 139).

Turbo-blower Developments

The other direction in which developments have been made is in the use of a turbo-blower. This has been universally used instead of a reciprocating compressor, in spite of its lower mechanical efficiency, because it can be built in large capacities without excessive size, and

because it gives a compressed steam free from oil. The combination of a turbo-blower and an evaporator has been given various pro-

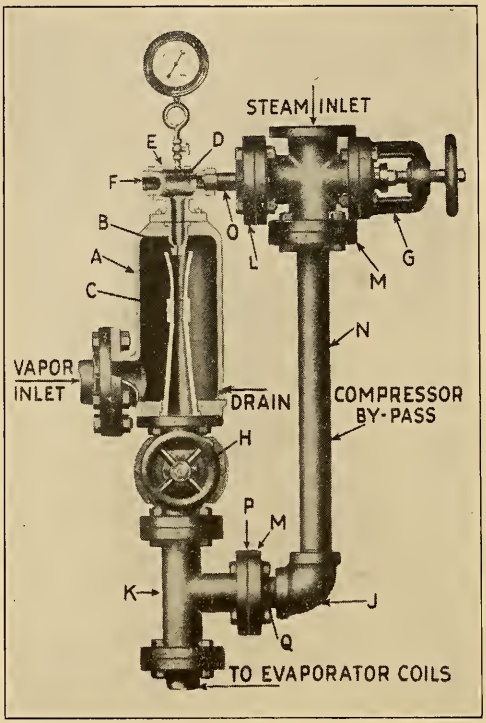

FIG. 8. The De Baufre Nozzle

prietary names, such as "auto evaporator," "heat pump," etc. They are rather popular at present, especially in Germany. (See 12, 16, 21, 38, 45.)

A well-known series of patents are those taken out by Soderlund and Boberg and assigned to the Techno-Chemical Laboratories, Ltd. (London) (2, 37, 105, 106, 108, 127, 128, 137, 141, 142). They have attempted both to isolate the effect of elevation of boiling point and to get a higher coefficient. This latter has been accomplished in their patents by imitating film evaporators of one type or another. For instance, in the evaporator shown in Fig. 12 (37 and 108), a high coefficient is supposed to result from liquor trickling down the sides of the tubes, distribution being through the device *i* (shown in

the insert) hung in the tops of the tubes. Feed enters the heat interchanger (being preheated by condensate entering at *d*), and goes to chamber 2, is circulated by pump 4 to chamber *h*. Vapors are withdrawn from *k*, compressed by the blower 5, and returned to *m*. In Fig. 13 (106, 128, 137) high coefficients are obtained by showering

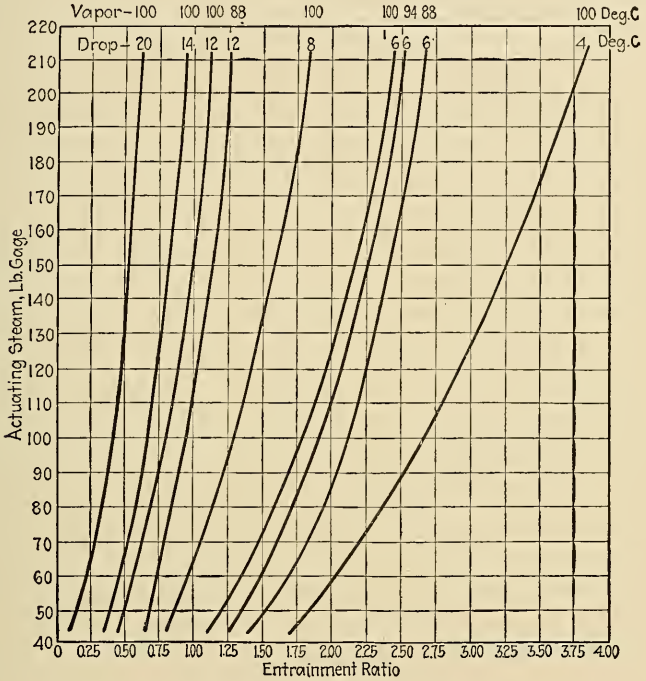

FIG. 9. Performance of Prache and Bouillon Nozzle

the liquid over horizontal tubes somewhat as in the Lillie evaporator; and at the same time an isolation of the effect of elevation of boiling point is obtained by running a series of bodies, vapor being stepped up by intermediate compressors to give the proper working temperature drop in each effect. Liquid is fed at 6, preheated by condensate in 7, and fed through float valve 21 into the liquor compartment. It is circulated over the tubes by pump 22, and a part is withdrawn from the first body by pipe 31 to the suction of pump 32 on the second body. The same system is repeated as often as desired. Partitions like 35 on the first body prevent too great mixing of the concentrated

liquor falling from the tubes with the thinner feed. A turbo-blower 25 takes vapors from the body and compresses them sufficiently to give a working temperature drop, and also to overcome the elevation in boiling point of the liquid being boiled. The patent claims ex-

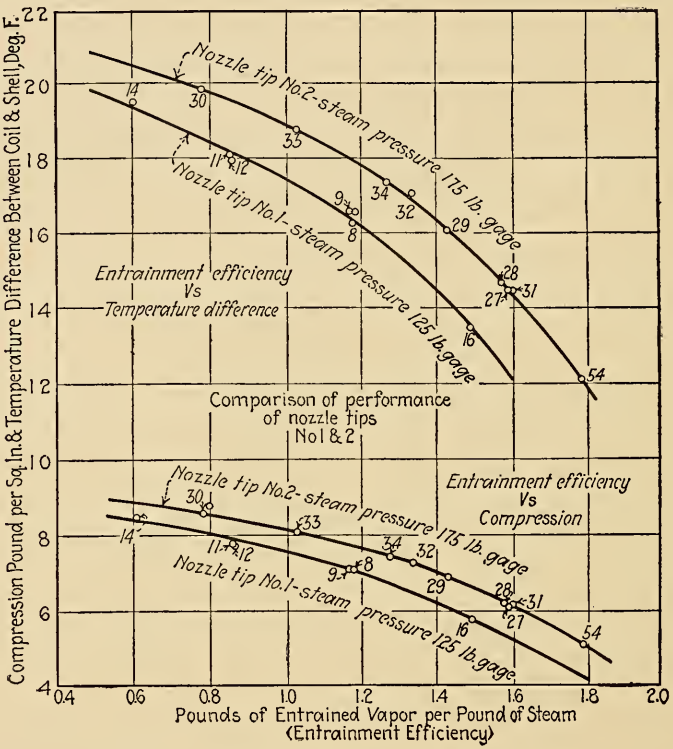

Fig. 10. Performance of De Baufre nozzle

pressly call for a working temperature drop of not over 3 deg. C. (5.4 deg. F.). Hence some type of film evaporator must be used, otherwise hydrostatic head would use up all the available drop. Part of the vapors go to the tubes of the first body, part to compressor 29, where they are given additional compression to correspond to the increased elevation of boiling point in the second body, and so on. The patent covers the same principle applied to vertical evaporators like Fig. 11, and also cases where compression is accomplished by nozzles.

There are a number of other patents covering similar devices

(113, 115, 122, 124, 132, 143, 146). In general, however, a patented or special apparatus is not necessary. A nozzle or turbo-blower may be adapted to any ordinary commercial evaporator (providing the proper precautions are taken to insure the necessary conditions for satisfactory operation). Such an installation is shown in Fig. 14. The only installations on which actual working data have ever been

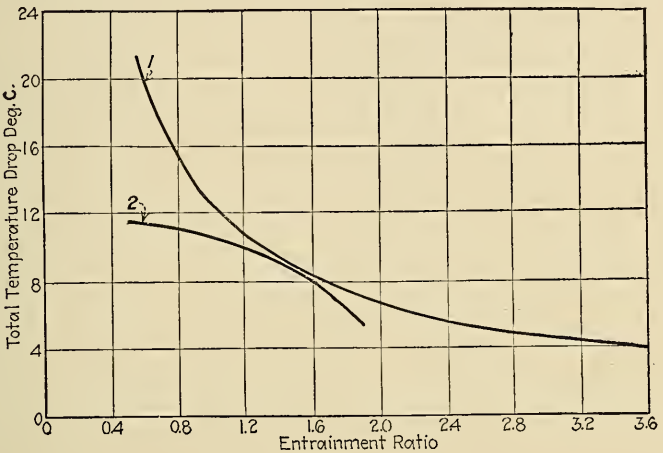

FIG. 11. Comparison of Nozzle Performance Using Steam at 175 Lb.

published are those in which there is no special feature in the construction of the evaporator itself. No information has been published to indicate that the various special and patented designs are successful or practical or necessary.

PUBLISHED DATA ON ACTUAL PERFORMANCE

Tusschen (41) and Carlsson (8) have reported results obtained on a small installation built by A. G. Kummler and Matter, Aarau. It evaporates NaOH solution. The same evaporator is described below by Wirth (46) (Apparatus *A*). A test by Stodola of Zurich Polytechnic showed 36.2 to 37.7 lb. evaporated per kilowatt-hour. Losses, which had to be covered by the direct addition of live steam, amounted to 12.4 per cent, of which 10.7 per cent was heat lost in thick liquor. This was not recovered because the solution could be used hot in the next step of the process. During these tests the elevation of boiling point was 3.6 deg. F. at the start and 12.6 deg. F. at the end of a batch.

Ombeck (29) reports tests on an evaporator with vapor recompression. The apparatus made distilled water for ice. The evaporator is not specially described, except that it had 1,260 sq. ft. of

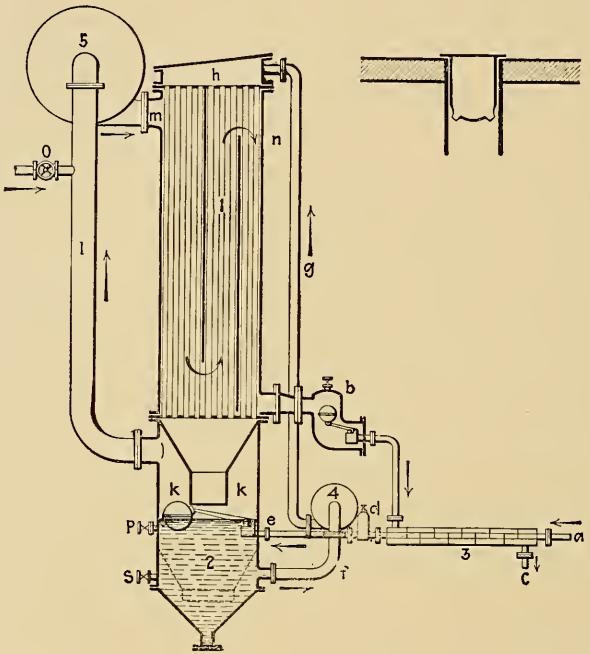

Fig. 12. Vertical Soderlund and Boberg Evaporator

heating surface. Vapor was compressed with a Rateau turbo-compressor. Raw feed water was softened and then preheated in a heat interchanger using the condensate as a source of heat. The principal results, abridged and converted to English units, are shown in Table I.

Runs 8 to 10 were made immediately after installation, runs 1 to 7 after 2 months' operation, and then runs 11 to 15 after cleaning. "Compressor efficiency" is the theoretical work of adiabatic compression divided by the actual power input.

It should be noted that the efficiency of the compressor increases, but the evaporation per kilowatt-hour decreases as the temperature drop increases. In some cases live steam had to be added to make up for losses in radiation, hot condensate, etc.; but in some cases the

TABLE I

Ombeck's Tests on Evaporator with Vapor Recompression

Run	Lb. Distillate Per Hr.	Vapors		Steam		Power Used, Kw.	Compressor Efficiency, Per Cent	Lb. Distillate Per Kw.-Hr.	Feed Temp. Deg. F.	Compressed Steam Temp. Deg. F.	Superheat, Deg. F.	Heat Added as Live Steam, B.t.u.	Apparent Temp. Drop, Deg. F.	Apparent Coefficient
		Temp., Deg. F.	Pressure, Lb. Gage	Temp. Deg. F., Calc. From Pressure	Pressure, Lb. Gage									
1	2,120	213.5	0.45	220.0	2.51	18.22	32.2	116	210.4	225.3	5.3	55,200	6.5	246
3	3,520	213.0	0.29	222.2	3.16	32.65	41.4	108	210.1	241.7	19.5	26,700	9.2	291
5	4,420	213.1	0.32	224.3	3.96	47.07	44.8	94	210.1	251.6	27.3	2,780	11.2	301
7	4,950	212.8	0.25	226.9	4.90	64.80	45.7	76	210.0	265.9	39.0	0	14.1	269
8	5,420	212.5	0.14	222.8	3.43	42.80	55.6	126	209.7	249.7	26.6	0	10.3	388
10	6,330	213.5	0.43	225.8	4.51	55.90	55.6	113	209.8	254.5	28.7	0	12.3	439
11	3,140	213.4	0.41	219.4	2.30	19.05	42.0	165	210.4	224.1	4.7	47,600	6.0	399
13	4,410	213.3	0.38	220.5	2.65	29.05	46.3	152	210.5	233.7	13.2	27,300	7.2	451
15	5,480	213.8	0.53	222.7	3.41	41.30	50.2	133	210.6	242.4	19.7	15,000	8.9	480

TABLE II

Wirth's Results with Compression Evaporators

Apparatus	Material Evaporated	Concentration (In Per Cent)		Batch or Continuous	Heating Surface, Sq. Ft.	Elevation of Boiling Point, Deg. F.		Power Used, Kw.		Lb. Evaporated Per Kw.-Hr.		Lb. Evaporated Per Sq. Ft. Per Hr. Start
		Initial	Final			Start	Finish	Start	Finish	Start	Finish	
A	NaOH	5	21	B	280	5.2	15.7	55.5	46.5	46.7	31.3	9.2
B	"Chemical Solution"	..	..	C	206	....	....	75.2	....	37.5	....	13.7
C	Sulphite Liquor	..	1.47 sp. gr.	C	3 x 475	....	....	....	....	55.2	....	23.4
D	NaOH	..	23	..	...	18	....	....	....	50.7	....	....
E	NaOH	..	31	..	384	....	41.5	....	....	25.4	....	2.87
F	NaOH	..	35	..	...	....	....	....	....	30.9	....	....

superheat from compression furnished more heat than was lost, so heat had to be discarded from the system by blowing off steam. It should also be noted that this is one of the simplest cases possible;

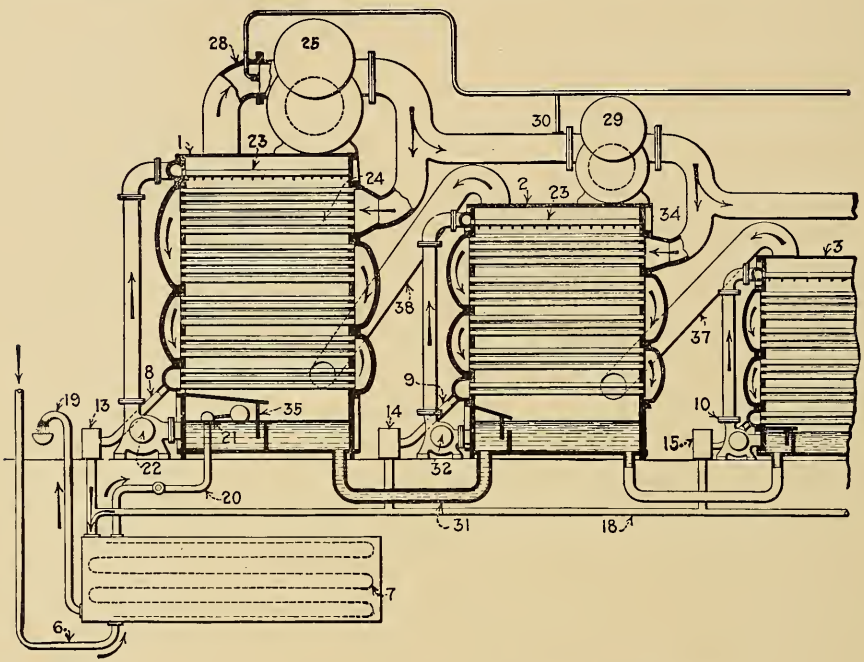

FIG. 13. Multiple Body Soderlund and Boberg Evaporator

boiling a non-scaling solution of low specific gravity and viscosity and with no elevation of boiling point.

Wirth (46)[3] has given details of a number of installations. A summary of his data will be found in Table II.

There is no special description of the evaporator construction. From the illustrations they seem to be ordinary vertical-tube evaporators with turbo-blowers. Case *E* is mentioned as the lowest practical rate for thermocompressor operation. Its small rating per square foot evidently means a very small temperature drop. Evaporator *F* has three bodies, all in series as to liquor and in parallel as to vapor. The compressor is in two parts; one part takes vapors from all three and compresses to give the temperature desired for steam to the first

[3] Wirth is connected with A. G. Kummler and Matter.

two. It delivers some of this steam to the second part, which compresses further for the third body. Mention is also made of a milk

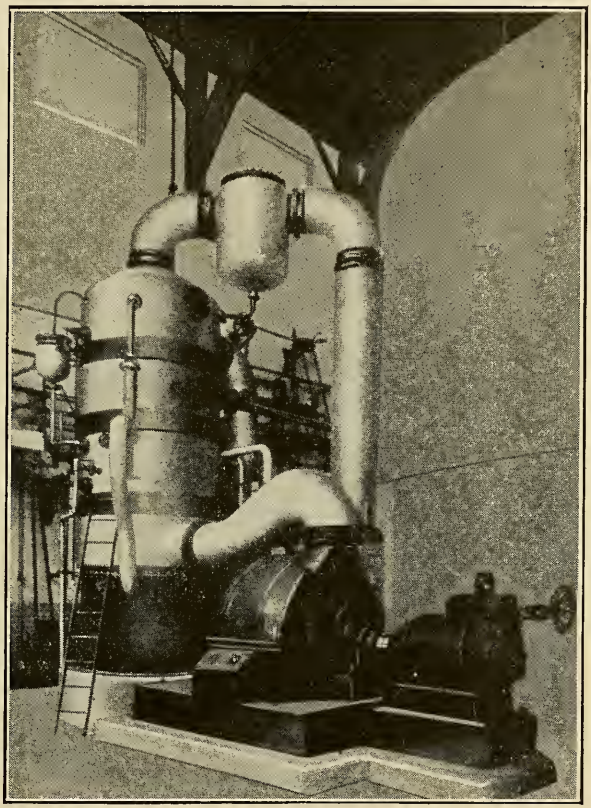

Fig. 14. Vertical Tube Evaporator with Turbo-Blower

evaporator, working with a boiling point of 50 deg., where the heat of compression more than covered the losses, so that heat had to be rejected.

General Theory

There have been a number of discussions of the general theory of vapor recompression. Of these the papers by Claassen (9, 15), Flugel (18), Holmes (20), and Wirth (46) are the most important.[4]

[4] See also 1, 32, 33, 47.

Nozzles

The nozzle systems are perhaps the easiest to discuss qualitatively. From the curves of Figs. 9, 10, and 11 any case that is apt to arise may be calculated. It is evident that for high efficiency (in the sense of vapor compressed per pound high-pressure steam used) it is necessary to work with a small temperature drop and very high-pressure steam. From Fig. 9 it will be seen that to get double effect efficiency (1 lb. vapor entrained per pound high-pressure steam) the total temperature drop may not be over 18 deg. F. for 100 lb. steam, 22 deg. F. for 150 lb. steam, or 22.5 deg. F. for 175 lb. steam. Ordinarily evaporators are designed to operate with 5 to 15 lb. steam. If a single effect evaporator with a nozzle compressor be compared with a double working between 10 lb. and 26 in. vacuum, we find that the double has a total available temperature drop of 100 deg. F. against, say, 20 deg. for the other. Hence, on material of no elevation in boiling point, the double would have five times the capacity of the single, twice the heating surface, and would require the same amount of steam, condensing water, and accessories.

On the other hand, if we assume that the plant has exhaust steam to spare, then the comparison is still more strongly in favor of the double. If a nozzle is used, either the power units must be run condensing or exhaust must be wasted. If an ordinary double is used, it saves either all the high-pressure steam used in the nozzle (if exhaust was available which would otherwise be wasted) or it saves all the condensing equipment and condensing water otherwise needed for the prime movers.

The best use for the nozzle is the plant where all exhaust from prime movers is used in the evaporators and, in addition, make-up has to be supplied as live steam. A nozzle may be substituted for the usual reducing valve on the make-up steam line; provided, of course, that the evaporator in question is a multiple effect with a small enough temperature drop in the first effect to make the nozzle efficiency appreciable. Here, again, attention must be paid to the rapidly decreasing efficiency of the nozzle as the steam pressure drops; because if the amount of make-up needed is variable, the nozzle will give useful results only when the throttle valve is wide open. Under conditions demanding less than the maximum amount of make-up steam, its capacity will be negligible. This has been discussed by Claassen

(9), who suggests several small nozzles in parallel to be cut in or out one at a time as the demand for make-up varies, but each to be either completely closed or wide open, never throttled.

Mechanical Compressors

Thermal Efficiency of Evaporators.—If the conditions are properly chosen and certain important considerations omitted, it is possible to show that vapor recompression systems are very desirable. For comparative purposes, let us assume that an ordinary evaporator uses steam at 5 lb. gage, and returns the condensate to the boilers at 180 deg. F. Then to regenerate 1 lb. of steam takes (1,155 — 180) or 975 B.t.u. Considering losses by radiation, heating feed, withdrawal of hot thick liquor, etc., let us assume that 1 lb. steam will evaporate 0.85 lb. water per effect. Then, for purposes of comparison, we will have as the performance of an ordinary evaporator:

Effects	B. t. u. Supplied in Boiler Per Lb. Evaporated
1	1,150
2	563
3	382
4	286

Let us also assume that the power used to drive the turbo-blower is generated in steam prime movers whose water rate is 20 lb. per kilowatt-hour. This rate, however, applies to steam of 160 lb. gage, which requires (1,195 — 100) or 1,095 B.t.u. to regenerate a pound. This assumes condensate returned to the boilers at 100 deg. F., because vapor recompression evaporators usually use a heat interchanger which cools the condensate and heats the feed. Ombeck's tests show 75 to 165 lb. evaporated per kilowatt-hour, or 3.5 to 8.25 lb. per pound boiler steam. This gives from 312 to 133 B.t.u. supplied in boilers per pound water evaporated. Wirth's data show 25 to 55 lb. evaporated per kilowatt-hour, or 875 to 400 B.t.u. per pound evaporated. Hence Ombeck's best tests correspond to 8.5 effect operation, and his poorest to 3.5 effect. Wirth's range from 1.5 effect to double effect efficiency. Such tests as Ombeck's and such reasoning as the first paragraphs of this article are the basis for the claims so often made of "multiple effect efficiency in a single body."

It should be pointed out again that Ombeck's tests were run on that combination of conditions which is the most favorable to recompression. Wirth's data represent much more general cases. The

efficiencies which have been calculated by advocates of thermocompression have not been confirmed by submitting operating data.

Capacity

The principal factors omitted by partisans of the thermocompressor are power generation and capacity of the evaporators. It is obvious that the turbo-blower must work on a small temperature drop. Thus Ombeck works with from 6 to 14 deg. F. Wirth gives no data, but his evaporation per square foot per hour indicates a similar or larger temperature drop. Ombeck evaporates 1.7 lb. per square foot with 6.5 deg. drop and 3.9 lb. with 14 deg. Hence, assuming similar coefficients, Wirth must be working with 10 to 60 deg. drop. This explains Wirth's lower efficiency rating. Most discussions have been based on a drop of 18 deg. F.; and Soderlund and Boberg specify 5 deg. F.

Now, ordinary evaporators usually run on about 100 deg. F. temperature drop. Hence, if the discussion has to do with an ordinary evaporator in single effect, the thermocompressor evaporator must have from two to ten times the heating surface to do the same work if the coefficients are the same. The lower figure for heating surface corresponds to so large a temperature drop that it would involve less than double effect efficiency. In an ordinary single effect evaporator the boiling point will be lowered corresponding to the vacuum. Hence there will be difficulty from increased viscosity, hydrostatic head, etc. The thermocompressor, working at atmospheric pressure, will have slightly better conditions, so far as these factors are concerned. Ombeck's coefficients, the only ones so far reported, are no larger than are regularly obtained under good conditions in ordinary evaporators.

A double effect will have an average temperature drop of 50 deg. per effect. Hence, if a thermocompressor could work with double effect efficiency on a 50 deg. drop with double the ordinary coefficients of heat transmission, it would do in one body all that an ordinary evaporator will do in two, both from the standpoint of thermal efficiency and of capacity. It would then remain to balance the cost of turbo-blower and driving unit on the one hand against the extra body of the evaporator and its condenser on the other. Similarly, the two methods are equal (except for difference in cost between the blower and the two bodies) if a thermocompressor could give triple effect efficiency on a 30 deg. drop with three times the ordinary coefficients. Wirth does not get triple effect efficiency in any case, and Ombeck

gets it only on a 14 deg. drop. There is no evidence to support the assumption of higher coefficients in evaporators using recompression. Hence it may be definitely stated that a thermocompressor will call for much more expensive equipment than an ordinary evaporator.

Superheat.—Another factor which may affect the capacity of vapor recompression evaporators is superheat in the compressed steam. Pure adiabatic compression will necessarily result in some superheat. Turbo-blowers have a mechanical efficiency of 60 to 70 per cent, according to size. This loss of 30 to 40 per cent of the power input should reappear as additional superheat in the compressed steam. Ombeck's blower had efficiencies of from 45 to 63 per cent, but his results show superheat only a little greater than called for by adiabatic compression. This was probably due either to long pipe lines between blower and evaporator, with the measurements made near the evaporator, or to faulty measurements of the temperature of the steam. This is a very difficult determination to make with even moderate accuracy. The superheat on large working temperature drops may be over 100 deg. F.

The effect of superheat has never been settled because, even with large amounts of superheat, the heat present as superheat is small, and is transmitted in the first fraction of the heating surface. No tests have ever been made where an appreciable part of the heat available for evaporation was superheat.

It is generally supposed that the presence of superheat considerably lowers coefficients of heat transmission from steam to metal. This comes from the well-known fact that permanent gases give up their heat very slowly. The actual data available are entirely insignificant, and it is still an open question as to what effect superheat may have. If it has any effect, then evaporators using turbo-blowers must suffer greatly and can not show normal coefficients of heat transmission.

In general, then, an evaporator using thermocompression will call for a larger investment in apparatus than an ordinary evaporator; and where it does not, it shows no special saving in steam.

Power Generation

Such a discussion as the above tells only half the story. No problem in evaporation should ever be discussed without including the question of power generation in the same plant. In the case above, of the ordinary evaporators run on 5 lb. steam, the steam would in

practice be exhausted from prime movers. Obviously, if the power demands of the plant are provided for and all exhaust used in existing equipment, adding a new evaporator would call for the generation of more steam and the comparison just made would need no modification. If exhaust steam were going to waste, a thermocompressor could not be considered, because the ordinary evaporator would run on exhaust, making no additional demands on the boilers. The thermocompressor would have to have high-pressure steam direct from the boilers.

Single Effect Operation

Consider a new department where both power and evaporation are to be provided and plans may be made for co-ordinating the two. The total amount of evaporation to be accomplished will call for a single effect only. In one case let us assume steam raised in the boilers at 160 lb. gage, expanded to 5 lb. in turbines, and sent to evaporators. The turbines generate power which can be used in the plant or sold. In the other case, let us assume 160 lb. steam raised in the boilers, part being used in condensing turbines to generate power equivalent to the power in the first case, and part used to operate evaporators. Let us base the comparison on 1 kw.-hr. under the first case, and consider that there is enough evaporation to be done to use all the exhaust there provided. The assumption made previously that 1 lb. steam to the first effect will evaporate 0.85 lb. of water per effect will still be made. The various possibilities are as follows:

Case *A*—1 kw. of power used, generated in non-condensing prime movers, exhaust to single effect evaporator operating on 100 deg. temperature drop.

Case *B*—1 kw. used, generated in condensing prime movers, additional steam used for single effect evaporator.

(1) Steam raised at high pressure, expanded through reducing valve for an evaporator which is same as in Case *A*.

(2) Same as (1), but expanded through a nozzle which compresses 1.2 lb. vapor per pound steam through an 18 deg. temperature drop.

(3) The additional steam generates additional power in condensing prime movers, this power being used to drive a turbo-blower.

(*a*) Blower gives 70 to 80 lb. evaporation per kilowatt-hour on a 14 deg. temperature drop (Ombeck).

(*b*) Blower gives 40 lb. evaporation per kilowatt-hour on a 25 deg. temperature drop (Wirth).

A comparison based on 40 lb. boiler steam raised would give:

	Case *A*	Case *B*			
		(1)	(2)	(3*a*)	(3*b*)
High-pressure steam to be raised.....	40 lb.	20 lb. for power 20 lb. for evaporator	20 lb. for power 20 lb. for nozzle	20 lb. for power 20 lb. for blower turbine	20 lb. for power 20 lb. for blower turbine
Power units.....	1 kw. non-condensing turbo-generator	1 kw. condensing turbo-generator	1 kw. condensing turbo-generator	2 kw. condensing turbo-generator, motor-driven blower	2 kw. condensing turbo-generator, motor-driven blower
5-lb. steam available for evaporators:					
Exhaust or expanded.....	40 lb.	20 lb.	20 lb.	None	None
Compressed.....	None	None	24 lb.	70–80 lb.	40 lb.
Total.....	40 lb.	20 lb.	44 lb.	70–80 lb.	40 lb.
Total evaporation....	34 lb.	17 lb.	37 lb.	60–68 lb.	34 lb.

A comparison based on 34 lb. of evaporation in all cases would give:

	Case *A*	Case *B*			
		(1)	(2)	(3*a*)	(3*b*)
Total steam to be raised.	40 lb.	60 lb.	36 lb.	30 lb.	40 lb.
Water for condensers:					
Power condensers.....	None	500 lb.	500 lb.	750 lb.	1,000 lb.
Evaporator.....	850 lb.	850 lb.	850 lb.	None	None
Total.....	850 lb.	1,350 lb.	1,350 lb.	750 lb.	1,000 lb.
Heating surface of evaporators.....	x sq. ft.	x sq. ft.	$3.7x$ sq. ft.	$4.8x$ sq. ft.	$2.7x$ sq. ft.

In order to make a clearer picture, consider a case in which the total evaporation to be accomplished is 1,000 gal. per hour. On a conservative rating the evaporator in Case *A* should have about 350 sq. ft. The steam consumed in Case *A* will be 9,800 lb. per hour (0.85 lb. evaporation per lb. steam), which corresponds to about 250 kw. power for the plant. Based on the preceding table, we shall have:

	Case *A*	Case *B*			
		(1)	(2)	(3*a*)	(3*b*)
Total steam needed per hour	9,800 lb.	14,700 lb.	8,800 lb.	7,400 lb.	9,800 lb.
Total water needed per hour	25,000 gal.	40,000 gal.	40,000 gal.	22,000 gal.	29,000 gal.
Heating surface	350 sq. ft.	350 sq. ft.	1,300 sq. ft.	1,700 sq. ft.	950 sq. ft.

Too many factors come in to make a hard and fast comparison of costs. The following table shows, very roughly, however, what may be expected in an average case. Overhead (interest, depreciation, repairs, etc.) is estimated at 20 per cent per year (300 working days). Labor is considered equal in all cases, and hence omitted. Steam is not brought into the cost, as its cost is too uncertain; but data for

	Case *A*	Case *B*			
		(1)	(2)	(3*a*)	(3*b*)
First cost:					
Evaporator and accessories	$900	$900	$3,300	$4,300	$2,400
Power unit and accessories	8,500	9,500	8,500	19,000	19,000
Blower or nozzle	.....	.....	500	14,000	16,000
Total	$9,400	$10,400	$12,300	$37,300	$37,400
Cost per day:					
Overhead	$6.30	$6.90	$8.20	$24.90	$24.90
Water	30.00	48.00	48.00	26.40	34.80
	$36.30	$54.90	$56.20	$51.30	$59.70
Excess cost over Case *A* exclusive of steam	.....	18.60	19.90	15.00	23.40
Steam saved over Case *A*, tons per day	.....	(Uses more than *A*)	12	29	0

steam consumption have been given and steam cost may be inserted as desired. Water is taken at 5c. per 1,000 gal.

Case $B(3a)$ is the ideal case, and will seldom occur; but if the conditions here represented exist, and if steam costs over 50c. per ton, this calculation shows a saving. Actual operating conditions will come much nearer $B(3b)$, and here there is no saving in steam and an increased cost of $23.40 per day. In other words, in the case apt to occur in practice, the turbo-blower saves nothing in steam and may be much more expensive to operate than an ordinary evaporator. This reasoning leaves out of account the more expensive labor to operate the turbo-blower evaporators, differences in piping and distribution, etc. If the solution has an elevation of boiling point, the case against the thermocompressor is still worse.

Multiple Effect Operation

Suppose the plant could not use 250 kw. of power, but that 80 kw. could be disposed of. This power, generated in a non-condensing prime mover, would give about 3,300 lb. exhaust per hour for Case A. This is about a third of that available in the previous illustration; but our 1,000 gal. of evaporation per hour could be now accomplished with this steam in triple effect. This case is rather abnormal, as the sizes of all equipment will come out small. Steam consumption and cost of equipment will be figured on the basis of commercially practical units, reduced to the conditions of the problem in proportion to the amounts handled (thus eliminating the excess costs of small units per unit capacity). The results will then be strictly comparable among themselves and with the case of single effect operation above. The triple used in Cases A and $B(1)$ is to work with a 20 deg. temperature drop in the first effect, and evaporate equal amounts in each effect. The single (used in the other cases) is to work on the same coefficient as the first effect of the triple.

As before, Case $B(2)$ is a nozzle compressor with an 18 deg. drop, Case $B(3a)$ a turbo-blower on a 14 deg. drop, and Case $B(3b)$ a turbo-blower on a 25 deg. drop. The efficiencies are also the same as before.

MULTIPLE EFFECT OPERATION

	Case *A* Triple	Case *B*			
		(1) Triple	(2) Single	(3*a*) Single	(3*b*) Single
Steam raised:					
Power	40 lb.	20 lb.	20 lb.	20 lb.	20 lb.
Evaporation		20 lb.	20 lb.	20 lb.	20 lb.
Power units and accessories	1 kw. non-condensing	1 kw. condensing	1 kw. condensing 1 nozzle	1 kw. condensing 1 kw. condensing and blower	1 kw. condensing 1 kw. condensing and blower
Steam for evaporation:					
Exhaust	40 lb.	20 lb.	20 lb.	None	None
Compressed	.....	.....	24 lb.	70–80	40
Total	40	20	44	70–80	40
Evaporation	135 lb.	68 lb.	37 lb.	60–67	34

135 LB. EVAPORATION AND 1 KW. POWER

	Case *A*	Case *B*			
		(1)	(2)	(3*a*)	(3*b*)
Steam:					
Power	...	20	20	20	20
Evaporation	40	40	73	40–45	80
Total	40	60	93	60–65	100
H_2O for condensers:					
Power, lb.	...	500	500	500	500
Evaporation, lb.	850	850	3,400	1,000–1,100	2,000
Total	850	1,350	3,900	1,500–1,600	2,500
Heating surface	$3x$	$3x$	$3.3x$	$4.3x$	$2.4x$

Then for a total evaporation of 1,000 gal. per hour as discussed under single effect operation, we would have:

	Case A	Case B			
		(1)	(2)	(3a)	(3b)
Total steam needed, lb. per hr. for					
Power	3,300	1,650	1,650	1,650	1,650
Evaporation	.....	3,300	6,000	3,500	6,800
Total	3,300	4,950	7,650	5,150	8,450
Total water used per hr., gal.	6,300	10,000	29,000	11,500	18,500
Total heating surface, sq. ft.	1,050	1,050	1,150	1,500	840

	Case A	Case B			
		(1)	(2)	(3a)	(3b)
First Cost:					
Evaporators	$2,600	$2,600	$2,900	$3,800	$2,100
Power units	3,300	3,450	3,450	3,450	3,450
Blower or nozzle	.....	.....	500	17,000	14,000
Total	$5,900	$6,050	$6,850	$24,250	$19,550
Operating costs per day:					
Fixed charges (20% per yr., 300 days per year)	$3.90	$4.00	$4.60	$16.20	$13.00
Water at 5c. per 1,000 gal.	7.50	12.00	34.80	13.80	22.20
	$11.40	$16.00	$39.40	$30.00	$35.20
Excess cost over Case A per day, exclusive of steam	.....	$4.60	$18.00	$17.60	$13.80
Excess steam used over Case A, tons per day	.....	20	56	22	62

Thus, on the assumption of power demands by the plant so large that exhaust enough is furnished to do all the evaporation in single effect, there is a possibility of so combining condensing power units and thermocompression evaporators to show a saving over the usual arrangement. This will be the case only when there is no scaling, no elevation of boiling point, no hot thick liquor withdrawn to the next step, etc. In the ordinary circumstances, thermocompression offers no saving as compared to a single effect, and will be still more expensive if compared to a multiple effect. In general, then, if the power demands of a plant are reasonably in proportion to its demands

for steam for evaporation, thermocompression is out of the question except where there is some unusual special condition.

Plants Using Purchased Power

The above discussion is based on the idea that the plant generates its own power. In case the plant generates no power, and central station or hydro-electric power is available, the comparison is different if the price of purchased power is low. Even with moderately expensive power, if the factory has no steam plant and supplies all its power demands with purchased power, it might be more convenient to put in a turbo-blower than to put in a steam plant. On a strict cost basis, however, power would have to be available at a figure very much under the cost of generation in the plant to make the thermocompressor arrangement economical.

Plants with Small Power Demands

The case which is most favorable to the thermocompressor is that of a plant whose evaporation problems call for the use of very much more steam than can be supplied as exhaust from their power units. Here we have four possibilities (after all the exhaust from non-condensing power units has been used): (1) Raise additional low-pressure steam for ordinary evaporators; (2) raise additional high-pressure steam and reduce it for the evaporators with a reducing valve; (3) raise additional high-pressure steam and send it to a condensing turbine driving a turbo-blower; and (4) raise additional steam, send it to a non-condensing turbine driving a turbo-blower, and use the turbine exhaust (along with the compressed vapor) in the evaporator.

Case 1 is evidently out of the question, as it takes very little more heat to raise high-pressure steam than it would to raise 5 to 10 lb. steam. Further, the chance of future needs for high-pressure steam would in any case warrant the slightly greater first cost of the boiler plant designed for high pressures. Let us then assume that the non-condensing turbine takes 40 lb. per kilowatt-hour, the condensing turbine 20 lb., that the turbo-blower will evaporate (*a*) 70–80 lb. per kilowatt-hour and (*b*) 40 lb., and that 1 lb. of steam will evaporate 0.85 lb. of H_2O per effect. Let us assume also that the amount of evaporation is such that a triple or quadruple effect evaporator would be used if Case 4 were adopted. Obviously, then, in Case 4 the first

effect would be enlarged. The evaporator may be looked on as a combination of a triple run on exhaust steam and a single with a thermocompressor. The single and the first effect of the triple happen to be combined in one shell, but it is simpler to think of them separately. Let us base our comparison first on 40 lb. of boiler steam, which gives us the following figures:

	Case 2	Case 3	Case 4*a*	Case 4*b*
Steam raised, lb.	40	40	40	Same as 4*a*
Power units	None	2 kw. condensing turbine and blower	1 kw. non-condensing turbine and turbo-blower	Same as 4*a*
5 lb. steam available for evaporators				
—exhaust	40	None	40	40
Compressed	None	140–160	70–80	40
Total	40	140–160	110–120	80
Lb. evaporated in single (from compressor)	None	140–160	70–80	40
In triple (from exhaust)	102	None	102	102
Total	102	140–160	170–180	142
Evaporator bodies	3 of x sq. ft. each	1 of $4.5x$ sq. ft.	1 of $3x$ 2 of x sq. ft. each	1 of $2x$ 2 of x sq. ft. each
Total surface	$3x$	$4.5x$	$5x$	$4.2x$
Lb. evaporated per lb. steam	2.55	3.5–4	4.2–4.5	3.7
Condensing water				
Turbines, lb.	None	1,000	None	None
Evaps., lb.	850	None	850	850

If a quadruple be assumed in Cases 2 and 4:

Lb. evaporated				
By compressor	None	140–160	70–80	40
By evaporator	135	None	135	135
Total	135	140–160	205–215	175
Condensing water:				
Turbines, lb.	None	1,000	None	None
Evaporators, lb.	850	None	850	850
Heating surface	$4x$	$4.5x$	$6x$	$5.2x$
Lb. evapd. per lb. steam	3.4	3.5–4	5.1–5.4	4.4

Assume an evaporator to remove 30,000 lb. of water per hour in quadruple effect. This would call for about 1,300 sq. ft. per effect,

and a steam consumption of 9,000 lb. steam per hour. If the data from the preceding table be converted to equal amounts evaporated, we shall have:

	Case 2	Case 3	Case 4*a*	Case 4*b*
Steam raised, lb. per hour	9,000	8,100	5,800	7,000
Water used, gal. per hour	23,000	24,500	14,500	17,500
Heating surface sq. ft. total	4,200	4,200	4,200	4,200
Hp. of blower turbine	.....	250	150	125
First cost of evaporator	$10,500	$10,500	$10,500	$10,500
First cost of blower and motor	.....	17,000	14,000	12,000
Total first cost	$10,500	$27,500	$24,500	$22,500
Fixed charges per day (at 20 per cent, 300 working days)	$7.00	$18.30	$16.30	$15.00
Water at 5 cents per 1,000 gal.	27.60	29.40	17.40	21.00
	$34.60	$47.70	$33.70	$36.00
Difference in cost from case 2 (excluding steam)	.....	+13.10	−0.90	+1.40
Steam saved over case 2, tons per day	.....	11	38	24

Hence, in the case where steam can not be supplied to the evaporators as exhaust from power units, but must be furnished from the boilers, it may be most economically supplied through a turbo-blower driven by a non-condensing turbine. This is in line with the general principle that the most economical method of using steam to produce both power and evaporation is a non-condensing prime mover sending its exhaust to the evaporating device.

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In the bibliography which follows every article to which a reference could be found is included, even though the original was not available. Some references were obtained from footnotes where the author did not cite his references accurately. This accounts for the incomplete citations in some cases.

Patents are arranged in numerical order except in the case of the English patents. These are arranged by years and numerically in each year. Where the same subject is covered by identical patents in different countries, full reference is made and subject given under the first entry, and succeeding notices refer back to that one. Foreign patents have not been examined other than by the literature references. All U. S. patents have been examined in the specifications themselves.

An asterisk indicates mention by title only, or an abstract so brief as to be useless.

The author wishes to express his indebtedness to L. A. Pridgeon, of the department of chemical engineering, University of Michigan, for much assistance in collecting the data on which this paper is based.

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103. 1,020,659. Prache & Bouillon. Aug. 18, 1908. Fr. 485,851, English 14,492, 1911; German 258,010. Crystallizing evaporator.

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Discussion

President Wesson: This is a paper which I think needs a little discussion.

Mr. Moore: Mr. President, that is a subject which I have been studying myself for a good many years, and I heartily agree with Professor Badger in his conclusions.

I might state here that the boiling point, except in those cases where the solutions combine, is dependent on the number of molecules in solution, and that the effect of concentration comes from molecules in solution, and therefore raises the boiling point of every solution that we have to do with industrially. For instance, if you take an ordinary sulphate liquor, or other liquors of that sort, you will have at least nine or ten degrees rise in the boiling point, just due to concentration itself. Or if you want to take an extreme case, take caustic soda for instance. The ordinary solution of caustic soda is 2 or 3 degrees above 212, but the ordinary point, the boiling point, of

caustic soda is about 300 degrees, so that you will see that you have there an enormous temperature difference.

Another thing—in many cases gases come off which are extremely destructive to the evaporator tubes, and so forth, and this is a very serious matter. I want only to touch on the matter, although it is a very serious matter.

The next question is the question of scale on the evaporator. The slight amount of scale makes a necessary temperature drop far beyond the efficiency gained. I want only to call your attention to a few of the outstanding objections to the thermal compressor. I made the statement the other day that I did not believe that one case out of a hundred would be economical with a thermal compressor, and Professor Badger corrected me and said he did not believe there would be one out of 800 where the thermocompressor would take the place of the ordinary evaporation. I think he was right, but I wanted to be conservative.

MR. HOWARD: Mr. President, I think it would be very interesting if Mr. Badger would make a comparison between a quadruple effect and a compression system, because he stated that the efficiency in the compression system in the case he took was about equal to a quadruple effect. The quadruple effect is a great deal more expensive than the single effect. It would be interesting to have the comparison made with a quadruple effect, and to have figures given as to the cost of a quadruple effect and the cost of a compression system of the same capacity.

PROFESSOR BADGER: I intended when I wrote this paper to include such calculations. But I can answer you simply. The capacity of the evaporator is a function of the total temperature drop. With single effect you might have a drop of 50 degrees Centigrade. If you put that across a quadruple effect, you will, roughly, need four times the heating surface of a single effect, because each effect is working approximately with one-fourth of the total temperature drop. But the heating surface per effect necessary to do the work is the same whether single effect or multiple effect.

Suppose you have a single effect apparatus working with a 5 degree drop with thermocompression, compared with a single effect working with 50 degrees drop, or ten times as much. You will see that a quadruple effect will have to have, to secure equal capacity, four times the heating surface of a single effect. The single works at ten times the temperature drop of the thermocompression evapo-

rator. Hence the single effect without thermocompression needs one-tenth the surface of the single with thermocompression. The quadruple effect would have to have four-tenths of the heating surface that the single effect with recompression should have.

There are, of course, radiation losses and temperature losses to be considered in practical operation, but offhand a quadruple effect apparatus working on a total drop of 50 degrees would have only about four-tenths the heating surface of a single effect apparatus.

That makes the problem rather complicated, and it brings the systems close enough together so that variations in the elevation of the boiling point and the balance between heat economy, on the one hand, and the first cost of apparatus, on the other hand, will throw the decision one way or the other. But the saving in favor of the thermal compression is only very little.

MR. HOWARD: I understood the principle, but what I meant was that it would be very desirable if calculations could be made of two typical cases, including the loss by radiation and other things.

PROFESSOR BADGER: Dr. Claassen in a paper which appeared last August made some calculations based on a beet-sugar factory. He assumed a quadruple effect apparatus with 50 degrees Centigrade drop, a total evaporation of 1,000 kilograms of liquor per hour in the first effect, 500 kilograms exhaust steam supplied, the other 500 being supplied by a turbo-compressor, this turbo-compressor to be driven by a steam turbine exhausting into the same effect. He showed that in such a situation, with one-half the steam supplied as make-up and the other half by recompression or exhaust from the compressor drive, there was no economy over a straight triple effect, and only 2 per cent economy over a quadruple effect. This calculation was based on a temperature drop for the thermocompressor as low as 5 degrees, which you seldom have. If you assume a compression in the thermocompression of 10 degrees, then the gain in the thermocompressor over a straight multiple effect is nothing.

MR. HOWARD: Wouldn't it be a fact that it would be more economical to use the most efficient type of turbine? Wouldn't you actually save by condensing the steam, thus using an efficient condensing turbine for the production of your power?

PROFESSOR BADGER: That question was thrashed over fully in the sugar industry nearly 20 years ago, and at least in the sugar industry it is considered axiomatic that where you have to generate power, and also do any heating or evaporating, the most economical method of using steam is to take power out of your steam down to the point

where that steam is available for evaporation, and then use the steam for evaporation. I do not think in any case where steam as exhaust is available for evaporation will you find it economical to use a thermo-compressor. If you are to have heat for evaporating, you can not afford to use a condensing prime mover.

MR. HOWARD: That would be true for multiple condensing systems, but would it necessarily work out that way for a compression system where the cost of power is the determining factor? Haven't you got to work out the exact figures to determine the answer? My suggestion was simply that figures made on two specific cases of typical apparatus would be very interesting and very valuable.

MR. CHUTE: On this subject I may give a few reminiscences. Many years ago I discovered in the classic work of "Foster on Multiple Effect" an article discussing this question of thermal compression, and the author gave an opinion far less favorable to it than that of Professor Badger. I know that he emphasized particularly the low thermo-dynamic efficiency of all prime movers which were necessary to recompress the steam. I presume that we have better prime movers now, so that this accounts for the more favorable impression of the professor. But Foster cites that in Switzerland there was, many years ago, a milk condenser which ran on this principle, because water power in Switzerland was very cheap and coal was very expensive, so that there might be like cases where it could be possibly used with economy and advantage.

MR. MOORE: In relation to Dr. Howard's remarks, I will say that I pointed out some years ago that there was very little economy in using steam anyway. The difference in operating a boiler at 100 pounds pressure and 150 pounds pressure is practically nil. That it is much easier to add another evaporator, and if you have exhaust steam to turn it into power, and if you have already sufficient power you can do it backward, and there is no harm in using exhaust for this purpose. In LaTuque we have power which we can get very cheaply, while coal is between $10 and $12 a ton, and a very poor grade of coal at that, very seldom averaging 12,000 B.t.u. a pound. Those conditions are very unusual and the small difference in operation of a boiler between 100, 125, and 150 pounds makes it a simple operation to generate all your steam by the original process and carry your operations on according to the local conditions which you happen to have. I have been all through this matter several times, and I agree with Mr. Badger in all the conclusions he has reached, absolutely.

EXPLOSIVES AND FERTILIZERS

By ALFRED H. WHITE

A contribution to the Symposium on Chemical Engineering and National Defense presented at the Baltimore meeting, Dec. 6, 1921

The intimate connection between explosives and fertilizers has been well known to the scientific world, but the roar of the stupendous explosion at Oppau in Germany a few weeks ago has perhaps accentuated it and has certainly brought vividly to the lay mind the possibility of the use of the same material for the two widely differing purposes. The mechanism of that unexpected explosion, which blotted out four hundred lives, is still a matter of conjecture, but it seems clear that a warehouse reported to contain 7,000 tons of a mixed salt of ammonium nitrate and sulphate, intended perfectly legitimately for fertilizer and believed to be entirely safe, unexpectedly exploded with all the violence of a high explosive.

The battle of Crecy has been famous for nearly 700 years, not so much because of the victory which the English won as because of the introduction of gunpowder and artillery as a decisive factor in warfare. It has been recognized for centuries that superiority in explosives and artillery was one of the strongest assets of a contending nation. As Napoleon cynically phrased it, "God is on the side of the heaviest artillery." Our own country has been hampered in all its major wars by lack of sufficient explosives. The Continental Congress urged the colonists in the days of the Revolution to make nitre plantations to supply the nitrate needed for gunpowder, and during the War of 1812 the earthen floors of Mammoth Cave in Kentucky were leached for the meager supply of nitrates stored therein. In our own Civil War the armies of the North were not nearly so hard pressed as those of the South, but many of the battles came to a standstill through exhaustion of ammunition. We remember the desperate state of the British armies in Flanders in 1914 and 1915, when they were subjected to the withering fire of the German batteries without possibility of an effective reply. When our own country entered the war in 1917 the first demand made upon us was for ex-

plosives. This was emphasized at the meetings of the Interallied Council in the fall of 1917, when it was brought out that Great Britain and France could supply artillery for all of our troops, as well as theirs, during the year 1918, but that they were in desperate need of explosives for their own troops. They specifically requested "that the American efforts shall be immediately directed to the production of propellant and high explosive powders on the largest possible scale." The reason for this shortage of explosives in France and Great Britain is found in the lack of raw materials in these countries. We think of smokeless powder as requiring cotton, nitric and sulphuric acids, and alcohol, and of the high explosives as requiring ammonium nitrate, together with toluene, sulphuric and nitric acids; but the fact which escapes our attention is that the raw material whose tonnage is greatest is one that does not appear at all in the finished product. It is coal. Each pound of smokeless powder requires nine to ten pounds of coal. The French had to import from 8 to 12 tons of raw materials for each ton of high explosives, and from 15 to 20 tons of raw material for each ton of smokeless powder. The expenditure of explosives during the World War was on a scale undreamed of before that time. Our American artillery, in their preparation for the attack on the St. Mihiel sector, fired two-thirds as many rounds of ammunition in four hours as the Union forces fired in four years during the Civil War.

The response that our country made to our allies' demand for explosives was a striking proof of the ability of this country to undertake large operations. Fortunately, most of the raw materials were present in abundance. Coal, cotton, alcohol, and sulphuric acid were obtainable in ample quantity. The production of toluene had to be stimulated, but the process of manufacturing it from California petroleum, which was developed to meet the emergency, was capable of furnishing many times more than the needed amount. The greatest shortage of material was in fixed nitrogen, especially in the form of nitric acid. The main source of the world's nitrate was in Chile, separated by a long ocean voyage from this country and from Europe, and the submarine campaign called for the diversion of every possible ship to carry troops and supplies to France. There was no certainty whether it would be possible to maintain the shipment of the amounts of nitrate required, nor, indeed, whether Chile would remain neutral and willing to furnish us the raw material. Germany had foreseen

that any war which involved Great Britain would immediately cut her off from supplies of nitrates, and she had guarded against this contingency, first by a large reserve stock, and second by the development of processes for fixation of the nitrogen from the air, which would render her independent of outside supply.

Germany's success in her nitrogen fixation program is a matter of common knowledge. She built plants which supplied her army with munitions and her soil with at least a part of its normal supply of fertilizer. No other country had deliberately planned for war, and so no other country had subsidized the development of this industry of nitrogen fixation. The ammonia from the coke ovens in the allied countries was entirely inadequate for the emergency, and England, France, and the United States all worked feverishly to install fixation plants. These could not be built in a day, and so the Armistice came with most of the plants uncompleted.

At the close of the war Germany had her plants as assets whose construction cost had already been largely amortized. They have been merged into one immense combination with government assistance, so that they are in a position to act as a unit and expend their energies where they are needed. In our own country the unfinished plants were scrapped and only two were retained. U. S. Nitrate Plant No. 1, built to produce ammonia by direct synthesis of nitrogen and hydrogen under high pressures—a modification of the Haber process—was not successful in its operation. U. S. Nitrate Plant No. 2, at Muscle Shoals, built to fix 41,000 tons of nitrogen a year by the cyanamid process, was entirely successful. Both these plants are being maintained in a stand-by condition pending final decision by Congress as to their method of operation, if, indeed, they are to be operated at all. Other developments during and since the war have contributed to make our condition of nitrogen preparedness much better than it was in 1916. The stimulation in construction of by-product coke ovens has doubled the amount of ammonia which may be produced in the United States from this source. Methods for oxidation of ammonia to nitric acid were developed during the war. Provided our country maintains a reasonable stock of nitrate of soda as a military reserve, these sources of ammonia production should allow us to supply the needful explosives for a defensive war. If we should ever be drawn into another cataclysm, we would have to construct new plants as in the last war.

If we had to face another such emergency, we would be better prepared, for the processes for nitrogen fixation are much better known than they were when we entered the war. The cyanamid process had been well developed before the war both in Europe and at Niagara Falls, and the plant at Muscle Shoals designed by the American Cyanamid Company represents the most advanced construction in these lines. The other important process for nitrogen fixation, the Haber process and its variants, reached a high development in Germany during the war. The one plant attempted in this country and constructed with government funds at Sheffield, Alabama, failed to operate satisfactorily. But the same private interests that designed this plant have, with the experience gained through the first venture, designed and constructed a plant at Syracuse, New York, which is stated to be producing 12 tons of anhydrous ammonia per day and to be operating very smoothly and satisfactorily. In case it becomes necessary for the government to construct synthetic ammonia plants, there is a pilot plant with trained personnel, whose services would, undoubtedly, be made available to the government for the national defense. From France comes the report that the famous French engineer, M. Georges Claude, has been successful in his daring attempt to produce ammonia synthetically, not at pressures of 100 atmospheres, or even 250 atmospheres, but at pressures of 1,000 atmospheres. This process, which works with inflammable gases in steel containers at red heat under pressures which are almost half of those set up in a cannon when fired, is certainly one of the most remarkable that has ever been attempted, and the success of M. Claude is further evidence that he is a chemical engineer of the very highest type.

It appears, then, that from the standpoint of raw materials for explosives our country is fairly prepared for national defense. The one raw material which has been lacking, fixed nitrogen, is now provided in reasonable amounts from our coke ovens, with the government plant at Muscle Shoals as an immediate reserve, and at least one private plant for direct synthesis of ammonia in successful operation.

Raw materials are, however, only one of the things needed for explosives. Even more essential is the knowledge of manufacturing processes which exists only with the maintenance of a trained personnel. It is probable that commercial explosives will always be manufactured in this country, and it may therefore be argued that there will always be an adequate nucleus of a personnel for war needs.

But is it probable that the manufacturers of commercial explosives will be leaders in the development of new materials which might be used in warfare? What kind of explosives will be used in the next war? The only answer which we are warranted in giving at the present time is that they will be unstable chemical compounds which must be synthesized with very great care and will almost certainly be complex organic compounds. The one type of factory which is always working with this form of synthetic organic compounds is that which manufactures dyes.

The connection between the dye industry of the country and the manufacture of poison gases has been frequently discussed. The relation between the dye industry and explosives has not been emphasized so much, and yet the operations of nitration are fundamental both to the dye industry and to the manufacture of explosives, and certain materials such as picric acid and di-nitro-phenol are in themselves explosives as well as products of the dye manufacturer. The relation of explosives to poison gas is so very close that it is not possible to say with certainty where one begins and the other leaves off, and I can not refrain from giving one specific instance of the ready adaptation of a dye works to the manufacture of poison gas.

The Badische Anilin und Soda-Fabrik of Germany has a capacity to produce 800,000 lbs. of indigo dye each month. Their process starts with alcohol, which is converted into ethylene and then into ethylene chlorhydrin. This latter product is heated with aniline and the oily residue is fused with caustic potash; from this fusion indigo is at once obtained by solution in water and oxidation by air. Were Germany to be drawn into war, this plant might be converted into a mustard-gas plant in scarcely an hour's time. The first two steps in the process are identical; in the third step sodium sulphide, a cheap chemical, is substituted for aniline, and the solution thus obtained is concentrated and treated in large tanks with hydrochloric acid. The oily product settling out at the bottom is the well-known mustard gas and may be drawn off at will.

This instance of the adaptation of a dye works to war purposes is cited partly to show the impossibility of chemical disarmament. Any nation which allows its dye industry to perish is in danger of destruction by an enemy which is prepared to unmask terrible agencies of destruction. These industries play an important part in our modern industrial organization, and unless the world is willing to do without

colors, and also synthetic medicinal products, these plants can not be wiped out. The only safe protection in this case is equality of preparedness.

Let us turn our attention from preparedness for war to preparedness for peace—to the measures necessary to maintain the fertility of the soil. The importance of the subject has been well summed up by Theodore Roosevelt, who, writing in the *Outlook* in 1912, said:

> "I have always been fond of history and of science, and what has occurred to Spain, to Palestine, to China, and to North Africa from the destruction of natural resources is familiar to me. I have always been deeply impressed with Liebig's statement that it was the decrease of soil fertility, and not either peace or war, which was fundamental in bringing about the decay of nations. While unquestionably nations have been destroyed by other causes, I have become convinced that it was the destruction of the soil itself which was perhaps the most fatal of all causes."

One of our most eminent American agriculturists, Dr. C. G. Hopkins, of the University of Illinois, showed in 1909 that one of their experimental fields which had been carried on crop rotation for seven years without fertilization decreased in fertility so that the crop of corn fell from 57.3 bushels to 33.9 bushels, and oats decreased from 74.4 to 25.9 bushels per acre. A check plot fertilized by addition of nitrogen and phosphorus increased its yields of corn over that given in the earlier years, and gave a crop of oats which, while not so large as in the first year of the test, was still 20 bushels greater than that given by the unfertilized plot.

The same authority cites the case of Russia, where the average annual yield of wheat for 20 years is 8¼ bushels to the acre, and where a decrease of only 2 bushels to the acre means a famine. He gives the following solemn warning, which is strikingly similar in import to that of President Roosevelt cited above:

> "With the exception of a few small countries, the record of our race is a record of ruined lands; and if we repeat, in the great corn belt of America, the history of the White Race in Palestine, in Southern Europe, in Russia, and in the eastern part of the United States, where shall our children go for bread?"

We in the United States are accustomed to think of our soil as a permanent asset, just as a generation ago we considered our petroleum, natural gas, and coal as permanent assets which did not need to be conserved. Yet the evidence is clear that even our richest soils

are deteriorating. The State of Illinois is, on the whole, one of the richest farming States in this country, and yet Dr. Hopkins has stated that if continuous crops of corn of 100 bushels per acre were grown on the Illinois farm lands, the supply of phosphate in the soil reached by the plow would be, not diminished, but totally exhausted in from 51 to 105 years. A corn crop of 100 bushels requires for the grain alone 100 pounds of nitrogen. Some of the poorer farm lands of Illinois contain only sufficient nitrogen in the surface soil for 46 crops of this sort, and none except the deep peat soils contain enough nitrogen in the surface soil to last more than 67 years. It is recognized that phosphates and other mineral fertilizers in some form must be added to the soil if its fertility is to be maintained. The nitrogen problem is, however, of more importance. The Illinois Agricultural Experiment Station states:

> "The nitrogen problem is the most important practical problem confronting the American farmer."

Although there is agreement among agriculturists and scientists as to the seriousness of the nitrogen problem in agriculture, there is not the same unanimity as to the best means of maintaining the nitrogen content of the soil. The early Roman writers on agriculture knew the value of leguminous crops as restoratives of soil fertility. The system of maintenance of a permanent system of soil fertility by proper rotation of crops and utilization of plant residues forms the basis of the system advocated by Dr. Hopkins for Illinois soils. However, the system requires more than the usual care, for their bulletin states:

> "The nitrogen of the soil, therefore, can not be maintained simply by incorporating a legume in the rotation, as is too often assumed. The proper utilization of the legume hay produced, and the return of its nitrogen to the soil, is a problem of utmost practical importance.
>
> "The use of a legume cover crop in wheat and oats also plays an important part in maintaining the nitrogen supply of the soil. The legume so used is probably of more importance really than its occurrence in the regular rotation."

It may be considered as proven that the nitrogen content of soil such as that of Illinois can be maintained without addition of a commercial fertilizer, provided sufficient attention be paid to the biological processes. The question is not, however, decided for other types of

soils and other methods of farming, and it is not settled whether the maintenance of the nitrogen content of soil through legumes is as economical as its partial restoration through commercial fertilizers. This is a question which can only be answered by a careful economic study and one which from its nature will have to be reconsidered with every variation in the cost items which enter into the computation. The recent increase in the value of farm lands and in farm labor have made it necessary to recast pre-war figures. Investigations made by the Farm Management Department of the Iowa State College of Agriculture in co-operation with the Iowa Farm Bureau Federation in 1920 showed that the average direct cost of growing an acre of wheat in Iowa was $18.19, of which almost exactly 50 per cent was labor and less than 10 per cent was charged to fertilizer. It may be noted that this fertilizer was merely manure and undoubtedly entirely inadequate to replace the nitrogen lost in the crop. The point to be emphasized is that this typical acre which produced 18.5 bushels of wheat had expended upon it $18.19 as direct charges, to which cost was added the figure of $16.80 for land charges, so that according to the computation the total cost of wheat was nearly $1.90 per bushel. Almost one-half was a fixed charge due to the land.

The Illinois system of permanent soil fertility as advocated by Dr. Hopkins dispenses with the use of commercial nitrogenous fertilizers, but gives no return at all to the owner of the soil during the fourth year when the land is wholly given over to the cultivation of clover, which is to be plowed under and from which not even hay is to be cut. If the direct cost of caring for the land during this year is estimated at only $5.00 per acre, and the land charge is to be $16.80 per acre, as estimated in the Iowa figures given above, it will mean that the cost of this method for replacing the nitrogen in the soil is $21.80 per acre. If nitrogen in fixed form may be purchased by the farmer at 15 cents per pound, he could buy 145 pounds for this sum, and if nitrogen could be purchased by the farmer at 10 cents per pound, which is not at all an impossible figure, he could buy 218 pounds of nitrogen. This would provide for the nitrogen removed by 218 bushels of corn, so that theoretically the farmer could grow a heavy crop of grain every year and be possibly better off financially than if he kept up the nitrogen content of his soil wholly by clover or other leguminous crops. The advantage to the nation is evident, for the product of the land during every year, instead of only three

years out of four, would add a potential one-third to our crop production.

It is not for the chemical engineer to decide what method of nitrogen replacement is best from the agricultural standpoint. It is proper for him, however, to consider how far he might meet a demand if it were made upon him.

The combined crops of wheat, oats, and corn in the United States amount to, roughly, 5,000,000,000 bushels annually. Each bushel removes from the soil about 0.9 pounds of nitrogen, so that the total annual loss of nitrogen from the soil in the grains alone is 4,500,000,000 pounds, or 2,250,000 tons of nitrogen. This is not an exorbitantly high estimate. Dr. Lipman, Director of the New Jersey Agricultural Experiment Station, was quoted in the hearings before the Senate Committee on Agriculture and Forestry (Senate Document 3390) as having estimated that the total annual loss of nitrogen from all land under cultivation in the United States, after making allowance for all returns to the soil, was between three and four million tons.

These figures are staggering, but the authority is good. Let us assume that we must return to the soil through commercial fertilizers, not the larger figure of 4,000,000 tons, but the smaller figure of 2,250,000 tons representing the loss in the grains alone. The tankage, cotton-seed meal, and other organic compounds now used account for only 4 per cent of this amount and their total is decreasing rapidly. The coke ovens and private plants for nitrogen fixation in the United States would make up less than 5 per cent. Imports of Chilean nitrate in the same amount as used for fertilizer before the war would furnish only 2 per cent. There is lack of agreement as to the future life of these Chilean nitrate deposits, just as there is lack of agreement as to the number of years before our petroleum resources in the United States will be exhausted. There is, however, general agreement that the life of both resources is limited, and that within one generation, or at most two, substitutes will have to be sought for the large uses of both these materials.

The organic wastes, coke-oven ammonia, and Chilean nitrates might together account for perhaps 11 per cent of the 2,250,000 tons of nitrogen called for annually to replace that removed from the soil by the grain crops. The remaining 2,000,000 tons would have to come from fixation processes.

There is only one really large fixation plant in the United States—that owned by the government at Muscle Shoals. It has a capacity for fixing 41,000 tons of nitrogen per year, and it would require 49 such plants to provide the nitrogen called for. Nitrogen fixation on this tremendous scale at a price which will render the product available for fertilizer is entirely impossible with our present technical developments. But is the prospect of such a demand merely a wild dream?

It was Sir William Crookes who, twenty-three years ago, in his presidential address before the British Association for the Advancement of Science, first called the world's attention to the probable exhaustion of the nitrogen of the soil throughout the world. I quote from his address:

> "Gradually all the wheat-bearing land on the globe is appropriated to wheat-growing, until we are within measurable distance of using the last available acre. We must then rely on nitrogenous manures to increase the fertility of the land under wheat, so as to raise the yield from the world's low average—12.7 bushels per acre—to a higher average. To do this efficiently and feed the bread-eaters for a few years will exhaust all the available store of nitrate of soda. For years past we have been spending fixed nitrogen at a culpably extravagant rate, heedless of the fact that it is fixed with extreme slowness and difficulty, while its liberation in the free state takes place always with rapidity and sometimes with explosive violence. . . . The fixation of nitrogen is vital to the progress of civilized humanity. Other discoveries minister to our increased intellectual comfort, luxury, or convenience; they serve to make life easier, to hasten the acquisition of wealth, or to save time, health, or worry. The fixation of nitrogen is a question of the not far distant future. Unless we can class it among certainties to come the great Caucasian race will cease to be foremost in the world, and will be squeezed out of existence by races to whom wheaten bread is not the staff of life."

A recent bulletin in *Science Service* by W. E. Allen, of the Scripps Institute of Biological Research of the University of California, calls attention to the effects of the famines in China on the development of that race. He says:

> "But deeper than that is the fact that the stress of famine has led to the destruction of every element in the population of the afflicted section except the one which is able to exist without shelter, without really protective clothing, and by the use of

> amounts of food incredibly small. When a people with such powers of endurance gets on a productive basis, who can hope to compete with them? Should they gain intelligent leadership what can stay their progress? Now, as always, some of the most pressing political problems center in the question as to the treatment to be accorded to a racial group or groups of tremendous physical endurance by a dominant race which has lost much of its capacity for endurance through prosperity, ease, or indulgence."

Sir William Crookes' solemn warning aroused the scientific world to the importance of nitrogen fixation, but after nearly a quarter of a century it is only a few in our nation who appreciate the vital importance of this problem.

The United States has been and is one of the most fortunate countries of the world—fortunate in its resources and fortunate in that its development came so late in the world's history that there is yet opportunity to conserve a fair share of its natural resources. Our nation in its infancy and youth was stimulated by the vitamines in the cream of our resources. We are fast getting down to plain milk, but are also matured so that we should still be able to thrive.

This discussion of the question of fertilizers and explosives has hinged largely on the question of supply of fixed nitrogen. From the military standpoint, our situation is much better than in 1917, and it would seem that our coke ovens, with their increased production, and the private plants for nitrogen fixation, with the government plants standing as a reserve, are sufficient to provide explosives for national defense.

The maintenance of our soil fertility stands out as a far larger problem. The United States will have to struggle to maintain its industrial preeminence and its high standards of living in the face of decreasing natural resources. Our soil fertility has been our greatest asset. As New England farms became unproductive their occupants moved to the Ohio and Mississippi valleys, where the soil produced in as rich a measure as the world has ever known. Even these marvelous soils are deteriorating.

The elements taken from the soil must be put back into it. The most important single constituent is nitrogen. Agriculturists have shown that it is possible to replace this by a system of crop rotation, but it involves an absolute lack of return from the soil during every fourth year. The increase in the value of farm lands has greatly

increased the expense of this process through the increase in fixed charges and has correspondingly increased the opportunity of the chemical engineer to produce fixed nitrogen at a price which can compete with this method of fertilization through biological processes.

The principles of nitrogen fixation are clearly outlined, but the developments are still in their infancy. The process of the synthesis of ammonia through direct combination of nitrogen and hydrogen presents possibilities and difficulties which challenge the best efforts of our chemical engineers, for this process has been called the most difficult chemical engineering operation which has ever been undertaken. The fixation of nitrogen can be accomplished as a military measure. Can it be accomplished so economically that it can produce the nitrogen needed by this country to maintain its soil fertility? That remains for the future.

In our study of national preparedness, we may list the raw materials for explosives as adequate, but the personnel which is to guide the future development is largely dependent on the fate of the dye industry and its related industries which deal with synthetic organic chemicals. The importance of a far greater supply of nitrogenous fertilizer is hardly yet recognized. The agriculturist through crop rotation and biological processes can meet the need in part. Can the chemical engineer develop the processes of nitrogen fixation so that the soil will remain productive and our children and our grandchildren live as comfortably as we do?

History shows that the fallen nations of the world either perished from exhaustion of the soil or were conquered by a hardier race after they had lost much of their original vigor through too much prosperity or indulgence. In either case they had failed in national preparedness. It was pardonable in the days of the dawn of civilization. It will be unpardonable if we, with our knowledge of the mistakes of the past and with the powerful weapons of modern science in our hands, make the same mistakes.

Discussion

President Wesson: Gentlemen, we have all enjoyed Professor White's paper very much. Is there any discussion?

Professor A. W. Smith: Mr. President, I think it is too bad for a paper so important as this to be abstracted so much. It is one of the most important papers that we have ever heard and it is to be

regretted that it has been so much abbreviated, since with our method of publication we shall not be able to see the text of it for a year. At least, that is a fair expectation from the past. I wish very much it might be arranged so that we can get it at an early date.

MR. HENRY B. COHEN: Muscle Shoals has been mentioned. I wonder if Professor White would give us his opinion of Henry Ford's offer. [Applause.]

PROFESSOR A. W. SMITH: Also, I wish he would give us his opinion of the process which the Germans are using, the Haber process for fertilizer, as well as the French method.

PROFESSOR A. H. WHITE: I am afraid I can not answer those questions in a minute.

PRESIDENT WESSON: Take all the time you want.

PROFESSOR WHITE: In answering them I am speaking, of course, as an individual, and purely from information in the newspapers, because I have no special information as to the negotiations with Henry Ford, or as to some of these other questions. But speaking in general from my previous knowledge of the Muscle Shoals plant, it seems to me that Henry Ford made a very liberal offer; in fact, a more liberal offer than any board of directors of a corporation would dare to make. He is taking a big chance and he may make a good deal of money. His chance of making money will be decided as a sales proposition and not on the technical issue of fixation of nitrogen. He is guaranteeing to pay the United States Government something like one million five hundred thousand dollars a year for ninety-five years, without any reservations. He also agrees to keep the Muscle Shoals plant in operation as a fertilizer plant and ready for the government in time of war, and agrees not to accept over 8 per cent profit on the manufacture of fertilizer in the government plant. His investment in that plant, according to the original proposal, if I read it right, will be only five million dollars. He may have to put in three million or four million dollars more to get it into shape for fertilizer works, but as his total capitalization will then be only ten million dollars, his overhead expense will be very low on a plant which originally cost seventy million dollars. Therefore, he could put out fertilizer at nearly cost and his income from that source would be small. He must also use the first one hundred thousand horsepower from that dam for fertilizer, and his opportunity to sell further primary power from dam No. 2 is not large. If dam No. 3

is built and put into operation, he could then sell additional power. And if he should sell, say, two hundred thousand additional horsepower in that district, which is at present but a small consumer, he would make money. If he can build up a second Niagara Falls in the next ten or fifteen years, he will make money from the sale of power, rather than from anything else. The government should get as good terms as it can from Henry Ford. Henry Ford will probably take care of himself. The dam ought to be completed. The money spent there, perhaps not wisely, ought to be saved and converted into an asset. The plant ought to be kept in operation and the Muscle Shoals dam ought to be built. The main item of disagreement between Henry Ford and the government officials seems to be the question of what the dam will cost. I don't believe anyone else will make a better proposition.

Now, in regard to the Haber process in Germany. From all the information we can get the indication is that it is working well, and that the explosion at Oppau was due to a mixture of the sulphate and nitrate of ammonia intended for fertilizer. Why it exploded no one knows. At least no information has been published. It has been said by some that it heated spontaneously. There may have been chemical action taking place. That material had set to a solid mass in the storehouse and it had been the custom to blast it out with dynamite. They were planning to blast that morning, and it is possible that the mass had become sensitive so that the small charge of dynamite set the whole mass off. It was certainly not an explosion in the Haber plant itself.

As to the plant at Syracuse, I have no knowledge of that except what has been told me. Dr. Nichols and the officials of the company have said that it is extremely successful and produces more than ten tons of ammonia every day without the application of external heat. If it is thermally self-sustaining, it is remarkable, because the Germans never reached that stage. The Germans had to inject air or use electric heating.

The word that comes from the Claude process is that it is developing very smoothly. Claude is a wonderful engineer. He promised to come over to our June meeting, and when his trip had to be postponed, he hoped to get here for this meeting. There is now some talk of his coming in February, and we hope when he does come that we will be able to plan for a meeting of the members of the American

Institute of Chemical Engineers, so that he may tell us what he has accomplished. When you think of a man working with combustible gases under such tremendous pressures and designing a plant so that it operates smoothly and easily, you can see what a wonderful achievement it is. I was told before I visited the plant that Claude had his bombs some thirty feet underground, and that the workmen went around in fear and trembling with their eyes on the nearest door. I went into the plant and it looked like the ordinary gas plant. The pipes, with their very high pressure, are very small, and although the gauge registered 1,000 atmospheres, the compressor was moving along just as smoothly and nicely as though it was pumping up automobile tires. Claude drew off some liquid ammonia for me, from that pressure of 1,000 atmospheres, and the valve worked as smoothly and as nicely as one could wish. It is a wonderful thing that he has done there, but how it stands commercially, of course, I could not ascertain. [Applause.]

THE UNIQUE DEVELOPMENT OF MODERN CHEMICAL STONEWARE

By PERCY C. KINGSBURY

Read at the Richmond Meeting, December 6, 1922

It is quite certain that the only material available for the first chemical experiments was clay ware molded to the desired shape and fired. Chemical ware may therefore be considered as dating from the beginnings of chemistry. As an industry, however, the manufacture of stoneware apparatus for chemical purposes is comparatively modern. The first plant devoted entirely to this industry was put into operation in 1836, although prior to this date several manufacturers of other clay products were making various shapes for the chemical industry as a side line, one manufacturer in Philadelphia having made chemical ware since 1816.

As might be expected, chemical ware has improved steadily in quality and workmanship during this time, although some of the ware made in Europe 50 years ago and which is still in service in this country bears very favorable comparison with much of the material sold to-day as chemical ware.

Early Products Limited by Potter

While there has been for many years a gradual improvement in the quality of this ware, it is only during the past 20 years or so that any serious effort has been made to manufacture anything except the simpler shapes. The chemical engineer of those days was compelled to design his plant to comprise only such shapes as the potter was willing or able to make. This is the reason for some of the inefficient apparatus seen around chemical plants to-day. A typical illustration of this is given in Fig. 1, which shows a vessel used for the absorption of hydrochloric acid gas in water. It is, as will be noted, a sphere flattened on the bottom. The purpose of the vessel is to offer a surface of contact between the gas and the absorbing liquid and to dissipate the heat of absorption by radiation from the exposed surface.

It will be observed that the path of the gas through the vessel is

extremely short, the gas is not brought down near the surface of the liquid, but is free to short-circuit across the top of the vessel, the surface of contact between gas and liquid is very small compared with the floor space the vessel occupies, and as regards the removal of the heat of absorption by radiation, it is a well-known fact that the sphere is the shape having the smallest surface for a given volume, so that in this respect it would be a physical impossibility to devise a more inefficient vessel. I have no doubt, however, that every member present can recall many installations in which this shape is used to-day for the absorption of hydrochloric acid and also for the condensation of nitric acid.

This is only one instance out of many that could be cited to illustrate how, to a large extent, the potter decided what kind of chemical ware equipment should go into a chemical plant.

At that time the engineer had no choice, as the various other materials that have been developed during recent years with more or less success for handling acids and other corrosive liquids were not then available. He had to put up with the inconvenience and loss due to the shortcomings of the ware manufactured in those days. The inertia of popular opinion is such that some prejudice persists in the minds of a few chemical engineers to-day, notwithstanding the fact that the reason for it has long since ceased to exist. I may say, however, that this prejudice appears to be confined to this country.

Extent of Stoneware Industry

According to the report of the U. S. Geological Survey for 1920, which has the latest figures available, chemical stoneware is manufactured in New Jersey, Ohio, Pennsylvania, New York, Massachusetts, Iowa, and California. The industry is, however, centered in New Jersey, one plant alone producing about 10 per cent more than the entire state of Ohio, which is the next most important producer. This New Jersey plant, which is the largest plant in the world devoted exclusively to the manufacture of chemical ware, produces as much as all the other plants in the United States put together.

What Is Chemical Stoneware?

Before considering the improvements that have been made in the chemical stoneware industry, let us first define this material.

Chemical stoneware may be considered as a skeleton or frame-

work of more or less refractory particles held together by vitrifying clays. It is obvious that the physical properties of this ware can be modified within comparatively wide limits by variations in the raw materials used for this skeleton, in the degree of fineness to which these materials are ground, and in the percentage employed in the mixture. At one extreme we have the coarse-grained chamotte bodies, which are of the nature of fire brick and which are used, for example, for conveying acid gases at a high temperature, as in a saltcake plant, where hydrochloric acid gas leaves the furnace at a temperature of

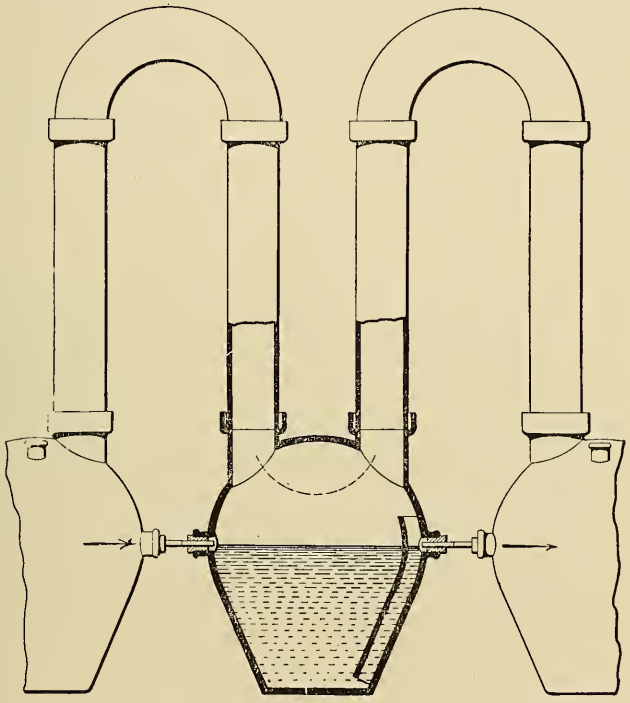


FIG. 1. Hydrochloric Acid Absorption Vessel

400 deg. C. or more. At the other extreme are the fine-grained porcelain-like bodies required for the large storage battery tanks used in power plants and for electrolytic cells. An infinite gradation of products is, of course, possible between these two limits and the selection and preparation of a suitable material to meet some definite purpose require considerable judgment.

The Clay Must Have Special Properties

The clay which forms the vitreous bond between the particles must meet certain very specific requirements. It must vitrify at a definite temperature—i.e., the temperature of the kiln—this being adjusted by mixing it with definite proportions of other fluxing materials. It must be very plastic so that it may be molded into the many different shapes the potter is called upon to make. There must be a considerable difference in temperature between the vitrifying and the fusing points, as otherwise the shapes made from it will soften and collapse or at least deform in the kiln. It must have considerable mechanical strength in the green state so as to be able to support its own weight before firing, when made up into large and often complicated forms. The shrinkage in drying and firing must be uniform, as otherwise it would be impossible for the potter to work to accurate dimensions, and the clay must be tough so as not to tear apart when subjected to the strain due to shrinking.

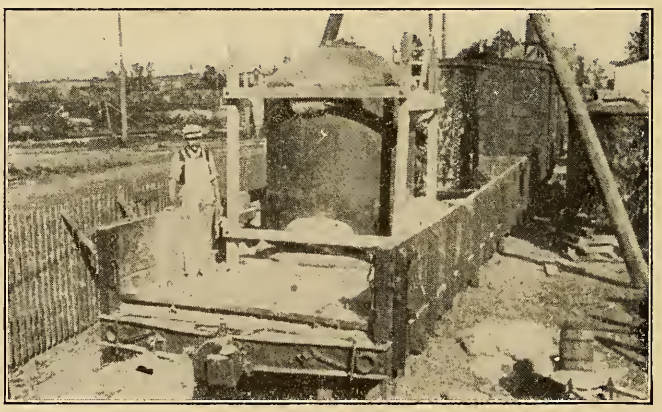


Fig. 2. 1,200 Gallon Acid Egg

No natural clay will meet all these requirements, and it is necessary to mix several kinds of clay in order to obtain the desired results. Clays suitable for the highest grade of chemical ware are not widely distributed, and for many years we imported about 80 per cent of our clays from Germany, notwithstanding the fact that our plants are located in one of the greatest clay deposits in the United States.

Preparation and Aging of the Material

The various clays are mixed in the desired proportions, washed and screened to remove soluble and other foreign matter. The excess water is then removed by means of filter presses. The other components are then added and the mixture passed several times through a mill in which it is kneaded thoroughly until it is perfectly homogeneous. The mixture is extruded from the mill in large blocks, which are then stored away for 2 years in a saturated atmosphere. This has the effect of greatly increasing the plasticity of the clay, and for some of our work where great plasticity is necessary, the body is stored for 5 years. The nature of this so-called aging action is still a matter of controversy. The popular opinion seems to be that it is bacteriological. It is known that it can be induced and accelerated by the addition of certain organic products, but after some experimental work along these lines we no longer use these expedients. When the clay bodies are ready for use, they are made up into the various desired shapes, due allowance being made for shrinkage.

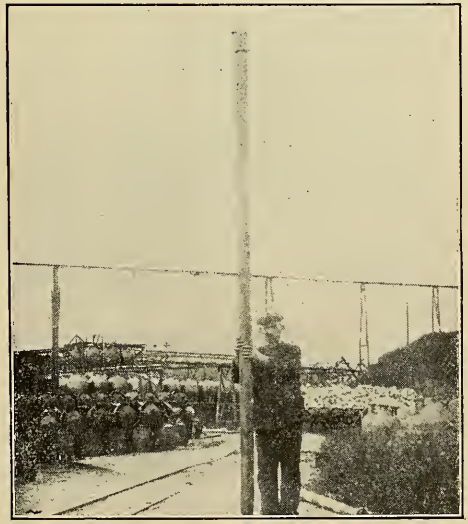


Fig. 3. Stoneware Pipe

Plaster of Paris molds are usually employed for this purpose, but many other methods are also used. Thus pipe and other cylindrical and prismatic shapes are extruded, some shapes are cast, a few shapes

are turned up by hand, and others are dry pressed. Where the quantities are large, as, for instance, in the case of carboy stoppers and Raschig rings for packing rectifying columns and scrubbing towers, elaborate automatic presses are used for this purpose.

Drying Must Be Carefully Controlled

After being shaped, the ware is dried. The most extraordinary precautions have to be taken at this stage of the manufacture. The shrinkage in drying is quite considerable, varying with the nature and moisture content of the body from 6 to 12 per cent linear. If the rate of drying of any particular shape is not uniform throughout, the uneven shrinkage causes deformation and often also internal stresses, the results of which are not apparent until after the manufacture is completed. In order to insure a uniform shrinkage at this stage, the drying has to be conducted very slowly, or a drier must be used in which the temperature and moisture content of the atmosphere are under control. Where complicated shapes are to be made or where extreme accuracy in dimensions is desired, a drier of this type is indispensable.

Salt Added During the Firing

The dry ware is packed in large kilns, which are then bricked up and carried to a temperature of about 1,300 deg. C. Just before the maximum temperature is reached common salt is thrown into the fireholes. The salt volatilizes and the vapor reaches every part of the kiln. A surface reaction takes place between the salt and the aluminum silicate of the clay body, sodium-aluminum silicate being formed, and dense fumes of hydrochloric acid pass out through the stack. I shall refer to this and other methods of glazing later on. When the maximum temperature is reached the kiln is cooled down very slowly by radiation until the contents can be removed.

The time required for firing a kiln depends on its size and to some extent on the nature of the contents. Our largest kilns require 3 weeks for a cycle—3 days for setting and discharge, 4 days for heating, and 13 days for cooling. This method of firing periodic kilns is extremely inefficient, practically all the heat being dissipated except a little that is used for drying green ware. For this reason we have recently installed at one of our plants a kiln divided up into chambers and furnished with an arrangement of flues so that the heat of the

chambers that are cooling off is utilized for heating those that are going under fire.

In the open kilns referred to above the products of combustion come into direct contact with the ware. In this reducing atmosphere the traces of iron in the clay impart a bluish-gray color to the body and a chocolate color to the glaze. In an oxidizing atmosphere the ware would be yellowish with a golden yellow glaze. White chemical ware, which is occasionally required for pharmaceutical and similar purposes, requires not only raw materials free from iron and other coloring matter, but the ware must be fired in a muffle kiln, as the atmosphere in an open kiln contains volatilized iron, which would stain the ware.

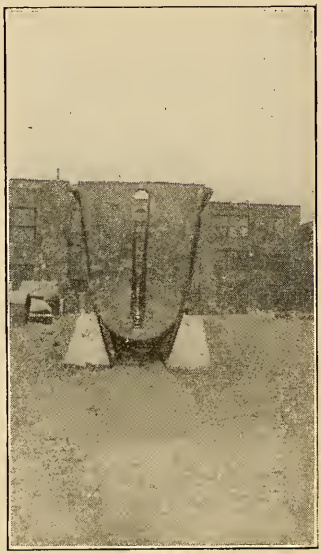
FIG. 4. Fitting for Fume Duct

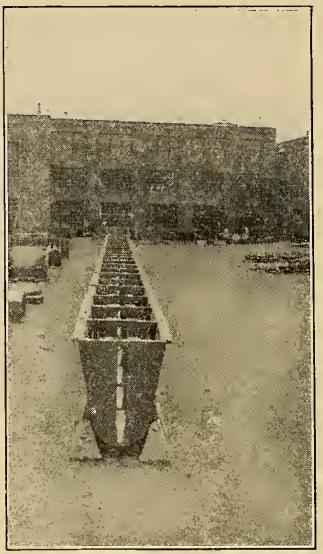
After removal from the kiln, the ware is tested and sent to the grinding shop if any further finishing is required. The material is quite hard and carborundum is mostly used for this purpose, although less expensive materials, some of which are of our own manufacture, are also employed.

Many of the manufacturing processes referred to above and much of the mechanical equipment is, of course, common to most clay-working operations.

The raw materials used in this industry are acid proof within the

usual limits for siliceous bodies, reference to which will be made later on, and they suffer practically no chemical change during the various manufacturing processes. There are, however, many problems of a physical nature met with in this class of work, the solution of which





FIGS. 5 AND 6. Special Stoneware Tank

has to be acquired in the plant and laboratory, as there is little or no technical literature on this subject. It is not my intention this morning, however, to discuss our manufacturing problems, but to direct your attention to the progress that has been made within recent years in adapting this ware to the requirements of the chemical industry.

PROPERTIES OF CHEMICAL STONEWARE

The possibilities as well as the limitations of chemical ware are best shown by a consideration of the chemical and physical properties of this ware. A typical analysis of chemical stoneware is as follows:

COMPOSITION OF MIXTURE 57

	Per Cent.		Per Cent.
SiO_2	73.23	K_2O	2.02
Al_2O_3	22.27	Na_2O	1.42
Fe_2O_3	0.58	Loss on ignition	0.06
CaO	0.58		100.16
MgO	Trace		

This ware resists the action of all acids excepting only those which react with the silica—i.e., hydrofluoric acid and hot strong phosphoric acid. Concentrated solutions of the caustic alkalis when hot also have some action on it. This action is, however, not considerable and caustic alkalis may usually be handled to advantage in chemical ware. As might be expected, a stoneware that is high in alumina resists the action of caustic alkalis much better than one that is high in silica.

Glazes for Chemical Ware

Chemical stoneware is usually glazed, the glaze, however, being merely a finish to give a smooth surface to the ware and not for the purpose of adding to the acid-resisting properties. As a matter of fact, the glaze is less resistant to chemical action than the body, and for this reason we are occasionally called upon to furnish unglazed ware. Under these circumstances a very dense body must naturally be employed. Some ware is manufactured for chemical purposes having a more or less porous body that depends for its acid-resisting properties on a heavy coating of a prepared glaze applied before firing by means of a brush or spray or by dipping. These glazes may be considered as clays with a low melting point which fuse in the kiln to a more or less homogeneous layer at the temperature of vitrification of the body. Such ware can scarcely be considered as chemical stoneware, as it offers no advantage over the various materials on the market coated with so-called acid-proof paints, varnishes, and enamels which become valueless as soon as there is the slightest imperfection in the exposed surface. There can be no question that salt glaze is much to be preferred for chemical work. A composition of this glaze is roughly as follows:

SiO_2	66.80	Na_2O	12.52
Al_2O_3	20.65		100.00

It is a sodium-aluminum silicate—i.e., a glass intermolecularly combined with the body so that it can not craze or peel.

Physical Characteristics

The physical characteristics of chemical stoneware are given in the following table:

Tensile strength, lb. per sq. in.	1,000–2,200
Compressive strength, lb. per sq. in.	25,000
Modulus of elasticity, lb.	6,000,000–9,000,000
Thermal conductivity, B.t.u.	0.55–0.6
Specific heat	0.2
Specific gravity	2.17
Coefficient of expansion (linear per deg. C.)	0.000003–0.000005

These are, of course, average values, as the physical properties vary considerably with different grades of ware. This is particularly true of the tensile strength. Thus the body we use for acid pipe lines has a tensile strength of 1,000 lb. per square inch, the body used for electrolytic work has a value of 1,700 lb. per square inch, and the

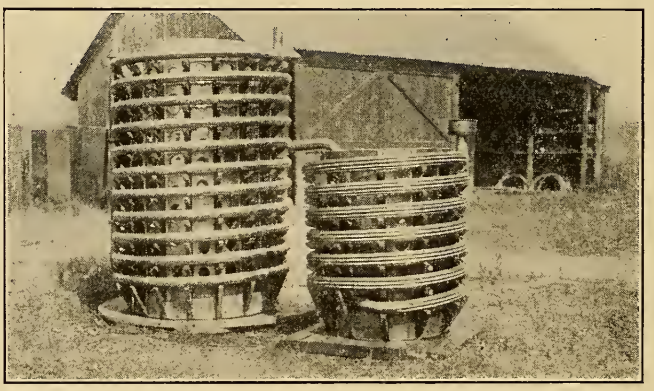


FIG. 7. Condensation Coil

bodies used for pump and exhaust fan impellers and for blowcases are much higher. We have tested an 18-in. impeller to 4,500 r.p.m. without bursting it—i.e., a peripheral speed of over 21,000 ft. per minute.

Attempts are frequently made to modify the physical properties of chemical ware by the addition of materials such as carborundum, various refractory oxides, etc. These products are placed on the market from time to time under fancy trade names and extravagant claims are made for them which have seldom been justified. This, however, opens a fertile field for the future development of this industry.

Practically any shape that can be made in metal or any other structural material can be duplicated in stoneware if due consideration is

given to the physical properties of this ware. The accompanying pictures will illustrate the possibilities that chemical ware offers to the chemical industry. In line with the general trend toward large-scale production we have been called upon to furnish equipment in as large units as possible. There is naturally a limit to the size to which clay ware can be made, but Fig. 2 shows a remarkably large vessel—undoubtedly the largest made in this country. It is the body of an acid egg or blowcase and was used for forcing a sludge into a filter press by means of compressed air at a pressure of 50 lb. per square

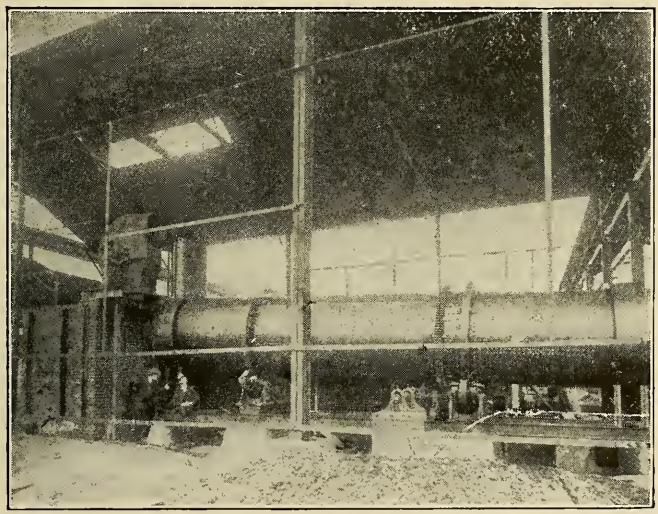


Fig. 8. Rotary Drier

inch. The vessel, which has a capacity of 1,200 gal., was, of course, protected by a steel shell on the outside. The sludge in this case was formed by treating carnotite residues with muriatic acid in the extraction of radium. Still larger shapes have been made in Europe, a 1,500-gal. vessel having been exhibited at a recent exposition in Dresden. The filter presses used in connection with the blowcase referred to were the usual wooden plate and frame presses. We designed and installed this equipment several years ago. It is interesting to record that we have now succeeded in making these filter presses also out of stoneware.

Fig. 3 shows a 4-in. pipe about 14 ft. long. One end is closed,

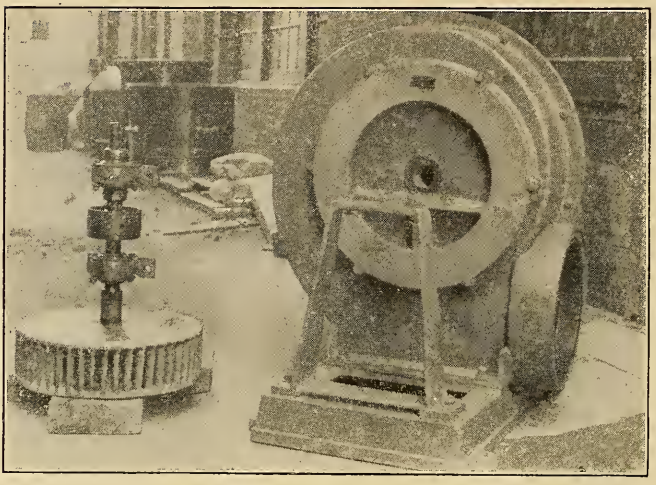


FIG. 9. Large Exhaust Fan

the other end is open and has a branch near the top with a flange under it. These tubes are used for cooling hydrochloric gas from about 80 deg. C. to about 15 deg. C. in the following manner: A stoneware tower has a perforated plate on top and twenty-six of these tubes hang in the tower supported by their flange on the perforated

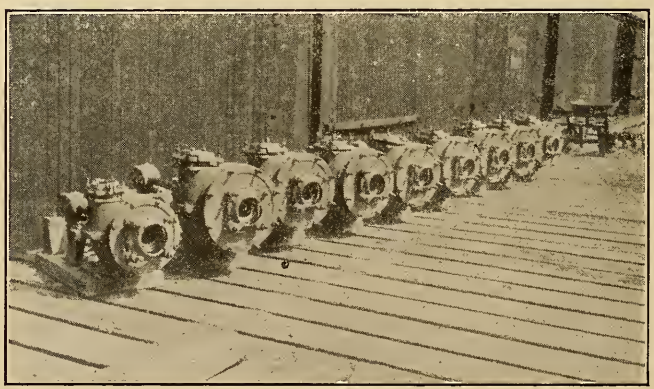


FIG. 10. Stoneware Pumps

plate. Each tube is cooled by water which is carried to the bottom by a pipe and which overflows through the branch at the top. I will

show you presently a picture of the complete plant in which this device is used. The idea is adaptable to all kinds of purposes in the chemical industry, but the tubes are not usually so long as in this case.

Fig. 4 shows part of a 48-in. diameter fume duct we manufactured a few years ago. This particular fitting is about 8 ft. high.

Fig. 5 is a tank we made during the war for the manufacture of radiators for airplane engines by electrodeposition of copper. I want you to note how accurately the slots match up. You will see it better perhaps in Fig. 6.

A stoneware coil (Fig. 7) usually impresses one not familiar with the manufacture of clay products. Given the right kind of body, however, they are not difficult to manufacture and will stand a remarkable amount of rough handling. The most usual size has a $2\frac{1}{2}$-in. tube with a wall $\frac{3}{16}$ in. thick and 80 ft. long. It is wound on a stoneware drum, but is not attached to it, so that the tube is free to expand and contract with change in temperature. We have shipped these coils all over the world. They are used principally for the condensation of nitric acid, for which they are ideal. They are also made as shown in the picture for cooling corrosive liquids. You will note that one of these coils has a corrugated cross-section for the purpose of increasing the cooling surface of the tube.

Fig. 8 shows a rotary drier with a cylinder about 20 ft. long. The entire cylinder was made of chemical stoneware and the flights were made integral with it. The feeding head was also of stoneware, as shown in the picture. The material to be dried was saturated with

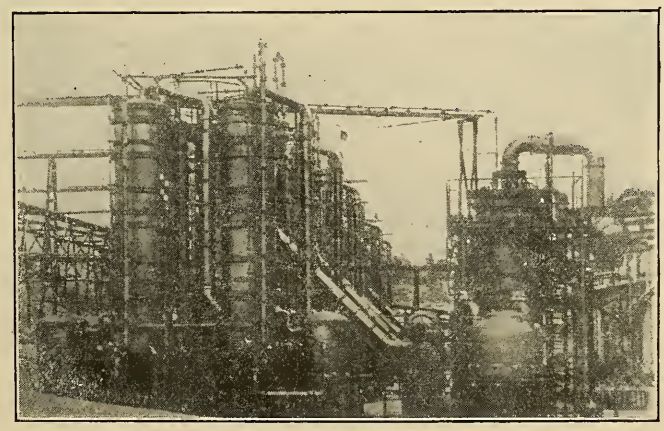


FIG. 11. Muriatic Acid Plant, All Stoneware

muriatic acid and every part of the machine coming in contact either with the moist material or the vapor had to be made of stoneware. The vapors were drawn off by a stoneware fan and condensed in stoneware towers.

A stoneware exhaust fan similar to that referred to above is shown in Fig. 9. This is the largest size we make to this design and will handle about 6,000 cu.ft. per minute. We furnished a very large

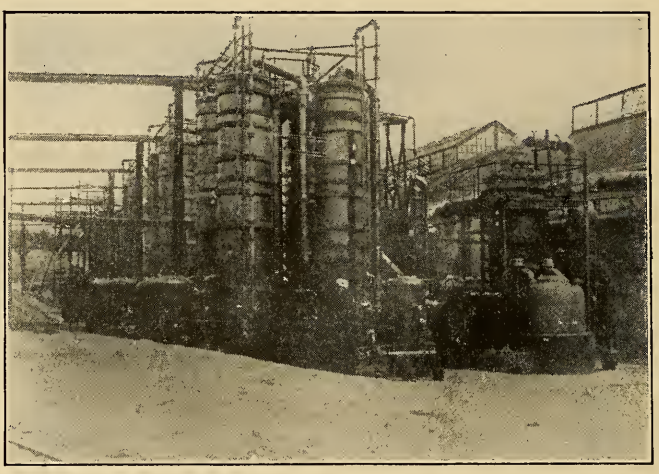


FIG. 12. Another View of Muriatic Acid Plant

number of these machines during the war for handling the oxides of nitrogen evolved from nitrating operations. The body and impeller—in fact, every part coming in contact with the gas—are made of chemical stoneware. I scarcely need say that a very high grade body is required for this class of work. The impeller shown in the picture is tested to 1,500 r.p.m. The smaller sizes are tested to 3,000 r.p.m.

Stoneware pumps (Fig. 10) are used for innumerable purposes around chemical plants and for handling every imaginable kind of corrosive liquid. They are also used largely for handling food products such as soup and vinegar, as they can be kept perfectly clean.

If stoneware chemical plant is to be thoroughly satisfactory, it must be carefully erected, and we therefore endeavor to use our own experienced men for this work wherever possible, whether the plant has been designed by ourselves or by our customers or their engineers.

Fig. 11 is a muriatic acid plant. This is the plant in which were used those 4-in. pipes 14 ft. long shown in Fig. 3. I want you to note that this plant has no protection whatsoever from the weather. The hydrochloric acid gas enters the pipe line at about 250 deg. C. and reaches the first tower at about 80 deg. C. The entire equipment is subject to zero temperature in winter and also to wind and snow and rain, but it has given no trouble whatsoever.

The Future of Chemical Stoneware

I have endeavored so far to show what has been accomplished in stoneware equipment for the chemical industry, and in conclusion would like to say a few words as to the future of this industry.

An important fact to be borne in mind is that although chemical stoneware is undoubtedly the best material for chemical plants handling corrosive products, yet it is no longer absolutely indispensable except in a few particular cases. No material has the general utility of stoneware, but for any specific purpose there is some other material that can be substituted for it except in a few special instances. In practically every case these substitutes have no advantage over chemical stoneware—in many cases they have very distinct disadvantages and they are almost invariably much more expensive. Every few weeks one or more of these new products is brought to our attention and most of them die a natural death after the usual comparative tests have been made, and this situation has acted as a stimulus to the chemical ware industry.

The production of chemical stoneware in the United States in 1920 increased 54 per cent over the 1919 production, and when the figures for 1922 are available they will undoubtedly show a still further steady increase. This is concrete evidence of the confidence of the chemical industry in American-made chemical ware which the manufacturer can easily retain if he will continue to improve his product and will base his sales propaganda on definite demonstrable facts and accurate data rather than on extravagant general statements and so-called "talking points."

Discussion

Vice-President Smith: This paper has opened up a wide field for discussion. I hope the members will take advantage of the opportunity.

Mr. Hugh K. Moore: I should like to ask Mr. Kingsbury how thin they find it practicable to make this stoneware, in, say, pipes up to a diameter of 4 to 6 inches? How have they succeeded in developing that?

Mr. Kingsbury: The thinnest wall we care to make on a pipe of this size is about three-eighths of an inch, but we can make it one-fourth of an inch if desired for some particular work. The danger there is rather in transportation than in manufacture.

Mr. Wadsworth: I should like to ask about the clays which are used as binders now. As I understand it, a great deal of that material was imported from Europe before the war. What is the situation in regard to that?

Mr. Kingsbury: Up to 1915 we imported about 80 per cent of our clays from Silesia. When we began to get into difficulties, we put the proposition up to the United States Geological Survey and we were successful in finding clays down South that were at least equal to German clays and for some purposes superior. They cost a great deal more, but I do not think we are likely ever to go back to the use of imported clays. Most of them come from Delaware, North Carolina, Tennessee, and Florida.

Mr. Jerome Alexander: I should like to ask if it is a fact that you can not find any other way of preparing your raw material than by a 3- to 5-year aging? It seems almost incredible that there is no way of facilitating that operation.

Mr. Kingsbury: That only refers to a small amount of our production. About the only amount of clay that we have to keep for that length of time is the clay that we need for making coils having a wall ⅛ inch thick, and this requires to be extremely plastic. Ordinarily we do not keep our clays more than two years, and sometimes less than that, depending on the use to which it is to be put.

Mr. Alexander: Has no scientific research been conducted to determine some means of maintaining this plastic condition?

Mr. Kingsbury: There has been a great deal of work done on it, but the opinions are equally divided. Some of them say it is bacteriological and others that it is physical.

Mr. Crosby Field: I should like to ask the speaker if there are any data available indicating the repairs or breakage of stoneware? In other words, what percentage of your business, or the business of your company, is represented by repairs and renewals?

Mr. Kingsbury: That is a hard thing to say. If a plant is properly erected and taken care of, there should be almost no limit—that is, as regards corrosion. There is a muriatic acid plant that is using some Austrian ware that was put in in 1873 I think, and is still in use to-day, and I am quite sure that if we dug that up and washed it up a little bit and put it in our yard, we could hardly tell it except for the color from the ware made yesterday. Most of the breakage is due to handling rather than the result of operation.

Mr. John M. Weiss: Will you tell us what is the cement used for making the joints in this material?

Mr. Kingsbury: That depends on the purpose for which you will use it.

Mr. Weiss: I mean for hydrochloric acid.

Mr. Kingsbury: For hydrochloric acid it depends upon which end of the process you are working on. At the hot end we use a silicate cement, and on the cool end we use either a tar and clay mixture or occasionally rubber dissolved in linseed oil and thickened up with some inert material such as ground-up silex or asbestos fiber.

Mr. Ernest D. Wilson: I should like to ask Mr. Kingsbury if he has overcome the difficulties of heating earthenware? I know we had a good deal of trouble when we tried one of your devices, although we proceeded against your advice. We were able to patch the tank up afterwards with cement and other things, but I wondered if you had overcome that difficulty?

Mr. Kingsbury: Do I understand it was a rectangular tank?

Mr. Wilson: No; a cylindrical tank.

Mr. Kingsbury: For that purpose we are prepared to furnish a vessel with a round bottom, so that we can make the wall thickness the same all the way through. With a cylindrical vessel, and still more with a rectangular tank, the edges and corners are 40 per cent thicker than the wall, and in heating and cooling it may tend to crack the tank if the change in temperature is sufficient.

Dr. Parsons: I should like to ask Mr. Kingsbury as to any research work done to increase the heat conductivity of stoneware. About two years ago a European told me what I thought was a fairy tale, and I have not yet changed my mind. I have tried to corroborate it in my two trips to Europe since. He stated that there had been developed by the Germans a ceramic material which had conductivity approaching that of metals; that they were able to use it for lining

metal apparatus; that they had a cement which would hold such tiles together; and that they were actually able to heat the outside of it with fire. He added that they got a conductivity through this ceramic material approaching that of metal. I am wondering what has been done along those lines.

MR. KINGSBURY: About the best results that have been obtained in that direction have been by the addition to the grit of refractory materials having a high coefficient of conductivity, of which, of course, the most obvious is carborundum, but outside of experiments along those lines I don't know of any work done in Germany that has achieved any material results. And I am sure I would have known of it if anything of the sort was done, because I am in touch with those people all the time.

THE PRODUCTION AND USES OF DUCTILE TANTALUM

BY CLARENCE W. BALKE

FANSTEEL PRODUCTS CO., INC.

Read at the Richmond Meeting, December 6, 1922

In the year 1801 Hatchett discovered the oxide of a new metal in a black mineral which he obtained from the British Museum. He named the metal columbium and the mineral columbite, because the mineral originally came from Massachusetts. A year later Eckeberg made a similar discovery while working with some new minerals from Sweden, and he named the new metal which he discovered tantalum. Subsequently a number of other investigators announced the discovery of new metals in tantalum- and columbium-bearing ores which were all shown to be mixtures of these two, and in 1866 Marignac developed his classical method for their separation, which depends upon the difference in solubility of their double fluorides with potassium.

The first mention of tantalum in the metallic form is that obtained by Berzelius. In 1824 he obtained a very impure product containing not over 60 per cent of metal, and having a specific gravity of 10, by reducing potassium tantalum fluoride with potassium. In 1902 Moissan produced a very hard and brittle form of tantalum high in carbon and having a specific gravity of about 12.8. In 1903 Dr. W. von Bolton, working in Germany, developed a process for the production of tantalum of sufficient purity to make it possible to produce drawn filament wire for incandescent lamps, and during the years 1905 to 1911 probably over one hundred million of these lamps were produced. This material as a filament wire was then replaced by tungsten.

About twenty years ago the writer became interested in these elements and devoted a number of years to the study of their various compounds and to the determination of their atomic weights. More recently, believing in the commercial value of this metal, an investigation was begun with the idea of producing the metal in commercial quantities. During the present year this investigation was brought

to a successful conclusion and it is now possible to produce tantalum characterized by high purity and capable of being worked into sheet, rod, or wire.

Occurrence of Tantalum

The elements tantalum and columbium are usually found associated with each other in their ores. The most important minerals containing these elements are columbite and tantalite, which are really iron salts of columbic and tantalic acids. Usually a part of the iron is replaced by manganese, and small amounts of titanium, tin, and tungsten are almost always present.

The mineral, samarskite, is a columbate and tantalate of iron, calcium, and the yttrium and cerium earths. Yttrotantalite is a columbate and tantalate of yttrium, iron, uranium, and the cerium earths. A number of other similar minerals also exist in more or less appreciable quantities. From the commercial standpoint, however, the first two minerals mentioned are the only ones of any importance. The mineral, tantalite, may contain as high as 80 per cent Ta_2O_5, and the best ore is probably that found in South Australia. The tantalum and columbium ores found in this country are almost entirely the mineral columbite, the element columbium being present in a larger proportion than that of tantalum. It is noteworthy that Greenland columbite is almost free from tantalum.

For the production of metallic tantalum tantalite is the most desirable ore and should contain at least 60 per cent of the oxide and only a few per cent of columbium oxide.

The first step involved in the production of metallic tantalum is the extraction of pure compounds of tantalum from the mineral tantalite. This involves the separation of the columbium which may be present.

There are a number of methods available with which to attack this ore. As the most suitable method for the separation of tantalum from columbium is through the difference in solubility of the potassium double fluorides, the method employed should be directed toward the easiest method of production of these compounds. The pulverized ore may be fused with potassium bisulphate. On leaching this fusion, the acids of tantalum and columbium remain insoluble and can be dissolved in hydrofluoric acid and treated with potassium fluoride, or the mineral may be fused with acid ammonium fluoride

and the tantalum precipitated from the solution of the melt by means of potassium fluoride.

A method which is more easily carried out on a large scale is the fusion of the finely pulverized ore with potassium hydroxide, which converts the tantalum and columbium into soluble columbates and tantalates. The filtered solution containing these salts may be treated with a mineral acid, preferably nitric or sulphuric acid, which precipitates the insoluble acids of tantalum and columbium. After washing, these are dissolved in hydrofluoric acid and the solution is treated with sufficient potassium fluoride to produce the double fluorides K_2TaF_7 and $K_2CbOF_5 \cdot H_2O$. These two salts are readily separated by crystallization, inasmuch as the columbium salt is about twelve times as soluble as the tantalum double fluoride.

The great insolubility of the tantalum double fluoride makes it quite easy to obtain this compound in a high state of purity by one or two recrystallizations. It is also possible to treat the solution of the mixed potassium tantalate and columbate directly with hydrofluoric acid which precipitates the difficultly soluble potassium tantalum fluoride, leaving all of the columbium in solution, provided the concentration of the solution is not too great.

This precipitated salt may be purified by further recrystallization. The purified potassium tantalum double fluoride may be considered the starting point for the preparation of metallic tantalum or any desired compound of this element.

The oxide of tantalum can be produced from this double fluoride by treating the solution of the salt with ammonia, precipitating the acid, which can be washed and then ignited to oxide.

Production of Metallic Tantalum

It is perfectly evident at the present time that the early attempts to produce metallic tantalum, involving such methods as the reduction of the oxide with carbon in an electric furnace, the reduction of tantalum oxide with aluminum by the Thermit process, or the reduction of the oxide by means of misch metal (mixed cerium earth metal), could not have given a product characterized by any degree of purity, and most certainly a metal which could not be subjected to any mechanical working.

Metallic tantalum powder can be produced by the reduction of the double fluoride with metallic sodium or potassium. It is impossible

by this process to produce a powder characterized by high purity. For best results by this method the reaction should be carried out in a vacuum, the boats or crucibles containing the mixture of double fluoride and metallic sodium or potassium being placed in a tube or furnace which can be evacuated before the mixture is raised to the reaction temperature.

The product from this reaction can be treated with water and mineral acids in order to free the metal powder as completely as possible from adhering salt and other impurities. This powder is then compressed into bars and subjected to heat treatment and finally fusion in a vacuum furnace, the high temperature of fusion eliminating the impurities which may be present. If this process has been completely successful, the fused metal will be found to be ductile and susceptible to mechanical working.

According to the literature and various patents, von Bolton produced tantalum filament wire by squirting a mixture of the lower oxide of tantalum and paraffin into wire and then heating this in a vacuum by alternating current. It is doubtful if any lamps were actually produced with filament of this character, as it was later found possible to produce drawn tantalum wire.

The most characteristic chemical property of tantalum is its unusual resistance to chemical corrosion. It is not attacked by hydrochloric or nitric acids or by aqua regia, either hot or cold. It is not attacked by dilute sulphuric acid at ordinary or more elevated temperatures, but appears to be slowly attacked by boiling concentrated sulphuric acid. Solutions of caustic alkalis do not attack the metal. Hydrofluoric acid seems to be the only chemical agent which will attack it, and in the case of very pure metal and very pure hydrofluoric acid the action is very slow. A mixture of hydrofluoric and nitric acids will attack the metal with avidity, causing it to go into solution as tantalum fluoride.

If tantalum is heated in the air, the surface becomes blue at a temperature of about 400 deg. C. and at a somewhat higher temperature nearly black. Above a dull red heat the white oxide is produced and the metal gradually burns. This metal combines with avidity with hydrogen, oxygen, or nitrogen. It will take up seven hundred and forty times its own volume of hydrogen, producing a very coarse-grained brittle product.

Tantalum containing dissolved gases will be harder than the pure

metal, and if their quantity is appreciable the metal may even be brittle, so that all annealing or heating operations with tantalum must be carried out in a vacuum. Tantalum burns readily when heated in chlorine gas, producing the volatile pentachloride. Solutions of chlorine, however, are without any action on the metal. Tantalum is not affected by any of the chemicals or antiseptics used in dentistry or surgery, probably without exception.

Physical Properties of Tantalum

It has been possible to produce metallic tantalum of an exceedingly high degree of purity, and to produce it in commercial quantities, having a purity of at least 99.5. The pure worked material resembles platinum very much in color and appearance. Its melting point may at present be taken as 2,850 deg. C. The specific gravity of the worked metal is 16.6. The pure metal is characterized by toughness and by its great ductility and malleability.

It has been found possible to reduce a bar of tantalum about ⅜ in. in diameter to wire of only a few mils in diameter without any intermediate heating to the annealing or equiaxing temperature, although the material is subject to strain hardening, resembling the more common metals such as silver or copper in this respect. Tantalum, however, resembles tungsten and molybdenum in that they may all be worked severely at temperatures below their equiaxing temperatures. Copper and silver may be worked at room temperature, but these metals become quite rapidly strain-hardened so that a further reduction makes it necessary to anneal the metal. Tungsten and molybdenum must be worked at elevated temperatures in the early stages, and if they are to be worked at room temperature in the finer sizes any operation corresponding to ordinary annealing must be avoided. Tantalum may be worked at room temperature to a remarkable extent without annealing.

The tensile strength of drawn tantalum wire may reach 130,000 lb., which is considerably more than that of hard drawn copper, nickel, or platinum, but less than that of molybdenum or tungsten.

The linear coefficient of expansion is more than that of molybdenum or tungsten and only slightly less than platinum. For this reason it is possible to seal tantalum into glass.

The electrical resistance is quite high, about eight times that of copper and about three times that of tungsten. The accompanying

	Tungsten	Tantalum	Molybdenum	Platinum	Copper	Nickel
Density	19.6	16.6	10.2	21.4	8.80	8.84
Atomic value	9.4	10.9	8.8	....	....	....
Tensile strength, lb. per sq. in.	490,000	130,000	260,000	Hard 54,000 An'l'd 42,000	62,000 35,000	120,000 70,000
Compressibility, kg. per sq. cm.	0.28×10^{-6}	50×10^{-6}	0.47×10^{-6}	....	0.76×10^{-6}	.....
Young's modulus of elasticity, kg. per sq. mm.	42,000	19,000	.....	....	.....	22,000
Melting point, deg. C.	3,350	2,770	2,550	1,755	1,083	1,452
Boiling point, deg. C.	.....	.....	3,617	3,907	2,310	.....
Specific heat	0.034	0.0365	0.072	0.0323	0.0936	0.1084
Linear coefficient of expansion per deg. C.	4.3×10^{-6}	7.9×10^{-6}	5.15×10^{-6}	8.84×10^{-6}	.....	13×10^{-6}
Thermal cond. in cal. per cc.	0.35	0.130	0.346	0.1664	0.7198	0.140
Temp. coefficient of expansion	0.0051	0.00335	0.005	0.0039	0.00393	0.0066
Elec. resistance, microhm per cc. at 25 deg., an'l'd.	5.2	14.6	4.8	9.97	1.87	6.4

table gives the physical properties of tantalum as far as they are at present known, and also those of a number of other metals in comparison.

High Chemical Resistivity Gives It Many Uses

In considering the possible uses for this metal we must take into account its high melting point, its resistance to chemical corrosion, and its tendency to absorb all of the common gases. We must also remember that we are limited by its relatively low temperature of oxidation. Tantalum seems to be a very desirable metal for the manufacture of certain dental instruments and dental spatulas, and undoubtedly for other dental and surgical tools or instruments. The metal is not attacked by any of the antiseptics or chemicals used and can be readily sterilized by heat. A surface film of hard material about as hard as agate can be produced on the metal by proper heat treatment. It will probably be found possible to harden the material throughout, thus combining all the advantages of tempered steel with absolute chemical inertness.

It has been suggested for use in the manufacture of pens and analytical weights. Its use in chemical laboratories and in the chemical industries as containers, parts of pumps and other equipment will undoubtedly depend upon the cost at which the metal can ultimately be produced.

Tantalum is suitable for cathodes in electrochemical analysis. In some respects it is more suitable than platinum. For instance, zinc may be plated directly upon the tantalum, as it does not alloy with the metal. Gold or platinum can be deposited upon the metal, as they can be removed by aqua regia without attacking the electrode.

Undoubtedly tantalum in the form of sheet, wire, or ribbon will find application in the manufacture of radio sending and receiving tubes. The property of tantalum of absorbing gases would seem to make the metal its own "getter" in vacuum tubes, and would tend to maintain the high vacuum required, particularly in the sending tubes. It would seem that some part of the lamp made of tantalum could be so constructed that at all times a portion of the metal would be at the proper temperature to absorb gas and would, therefore, tend to maintain a vacuum equilibrium within the bulb.

Use of Tantalum as an Electrolytic Valve

Tantalum has interesting possibilities on account of its property of acting as an electrolytic valve.

If two plates of bright tantalum metal are placed in an electrolyte and the two plates connected to an electric battery, there is an instantaneous flow of current similar to that between plates of the better known metals. Within a few seconds the current flow will drop to a very small comparative value, providing the battery voltage is not too high. The order of the current flow will become that of 1 milliampere and less with impressed direct current voltage up to 75 volts when sulphuric acid of the strength ordinarily used for storage batteries is the electrolyte. This drop in current flow will be accompanied by the formation of a film on the tantalum anode, presumably of tantalum oxide. This film often shows beautiful iridescent colors.

If a tantalum plate and a lead plate are placed in an electrolyte and a source of alternating current of the usual commercial frequency is connected to the tantalum and lead plates, the current flow in one direction will be almost entirely shut off and a pulsating direct current will be obtained. In such a set-up this flow of current is accompanied by electrolytic action with evolution of hydrogen gas at the tantalum and oxygen at the lead. The action of the tantalum is, therefore, such that electrons are permitted to flow from the tantalum to release hydrogen ions, but are prevented from passing from oxygen ions into the tantalum.

The current derived from this apparatus may be utilized for charging storage batteries, for the electrodeposition of metals, and various other electrochemical actions requiring a direct current.

It is possible, by using two tantalum electrodes in a single cell, so to rectify the current that both half waves of alternating current pass in the same direction. This current may be smoothed out by a suitable series of inductances and capacities to give what is practically a constant direct current.

The efficiency of tantalum as a valve with respect to leakage of the current varies with the impressed voltage, with the electrolyte, current density, etc. Due to the fact that tantalum is very inert toward the chemical action of solutions, there is a wide choice of electrolytes and the life of the tantalum appears practically unlimited.

For a charging set-up with a 6- to 8-volt battery the energy effi-

ciency is approximately 33⅓ per cent, which compares favorably with rectifiers of the hot and cold electrode type and the mechanically vibrating rectifiers.

The tantalum battery charging rectifier is noiseless in operation, has no moving parts, and requires attention in only one matter, which it has in common with the storage battery itself—that of distilled water being added to replace evaporated and decomposed water of the electrolyte.

In addition to functioning directly as a rectifier for obtaining continuous current, apparatus built along similar principles may be used for electrolytic condensers and electrolytic detectors and possibly lightning arresters.

Among other metals which have this property of valve action more or less in common with tantalum are magnesium and aluminum. However, owing to the ready susceptibility of both these metals to chemical corrosion, they have not proved very suitable as sources of direct current. Condensers and lightning arresters for high potential transmission lines are commercially used with aluminum plates.

Discussion

Vice-President Smith: This paper on tantalum is before you for discussion.

Mr. Hugh K. Moore: There are several metals which, while inert to aqua regia, when used as an anode, will not stand nascent chlorine such as you have in an electrolytic cell. I should like to know what is the effect of using tantalum as an anode, say, for instance, in electrolyzing salt brine?

Mr. Balke: It works beautifully for about two seconds, but you can not use it longer than that, and that really is the reason it acts as a rectifier.

Mr. Moore: I was thinking of using it with direct current.

Mr. Balke: The current drops to nothing after just about that long.

Mr. Moore: Is the hydride that you speak of more of the nature of palladium hydride? Will it vary up and down in its content of hydrogen so that you can use it as a catalyzer? For instance, assume that it is $Ni_3(OH)x$, you can rejuvenate your hydrogen. If you take all the hydrogen out, you can not rejuvenate it; but if you take part

out, its content will go up and down and you can revivify it. How does that work mechanically?

MR. BALKE: You can remove the hydrogen by taking the gas out, but I do not think you can get it all out.

MR. MOORE: I believe I did not make myself clear.

MR. BALKE: To get any of the hydrogen out, if that is what you mean, it requires a temperature of over 2,000 degrees Centigrade.

MR. MOORE: To get any of it out?

MR. BALKE: Yes; any appreciable amount.

MR. MOORE: That settles it. Is that on the market now as a commercial article?

MR. BALKE: Yes; in the form of small sheets and in rods and in wire.

MR. MOORE: What would be the approximate cost compared, say, with gold or platinum?

MR. BALKE: The base price is about one-half that of gold. The German price before the war was $1.00 a gram. This is worth one-half of the price of gold, 30 cents or 40 cents a gram.

MR. MOORE: Have there been any methods devised of casting it into cylinders or squirting it into cylinders?

MR. BALKE: Nothing has been done along that line. We have only been able to make the metal in workable form for three or four months and there is an immense amount of work to be done in producing it in larger quantities—that is, a larger amount in a given piece.

MR. MOORE: Can you attach it to iron? Can you spot-weld it on to iron as the protective coating of a propeller, for instance?

MR. BALKE: That has not been tried, but from the fact that we can spot-weld it to itself I think it could be done.

MR. MOORE: Has it been spot-welded to any other metal?

MR. BALKE: That has not been tried. We can spot-weld two pieces of tantalum, just as in the case of steel.

MR. MOORE: There are several pieces of mechanical apparatus which, if they could be protected with a thin sheet of tantalum at $1.00 a gram, it would not be prohibitive. It would have to be attached in some way to a metal so as to take up the basic strength on the cheaper metal, just using it as surface protection from certain gases, and that is the reason I asked the question.

MR. BALKE: That was one of the ideas that I originally had in mind when I began work to produce it in large enough pieces so that

it could be used, for instance, in centrifugal or acid pumps. If such a piece of equipment was once made, it would be practically an eternal proposition so far as chemical action goes.

MR. MOORE: What is its action under heat and cold? Does it tend to crystalize or does it take up expansion and contraction readily without tendency to fatigue?

MR. BALKE: The metal would burn up completely in air before it would be hot enough to cause any change in the covering. We have done only a few experiments in spinning, but it draws very nicely and I see no reason why it can not be handled like almost any other metal.

DR. ARTHUR C. LANGMUIR: If I understand you rightly, tantalum is a perfect substitute for platinum, provided it is heated in a vacuum?

MR. BALKE: I think it is a perfect substitute for all work that you can do before oxidizing.

DR. LANGMUIR: In a vacuum?

MR. BALKE: Oh, yes; in a vacuum.

MR. LANGMUIR: Then that suggests to me that there will be on the market soon a furnace for heating exclusively in vacuum.

MR. BALKE: That is something I had not thought of.

DR. LANGMUIR: You spoke of a vacuum furnace and I wondered if it were practicable in analytical work?

MR. BALKE: There is no reason that it could not be done.

MR. CROSBY FIELD: Under identical conditions of electrolyte and temperature, how does the volt-ampere characteristic curve compare with aluminum? And, secondly, I want to ask whether the working film of the tantalum oxide or hydroxide, or whatever it may be, is of the same magnitude as that of the aluminum film, about $\mu\mu$?

MR. BALKE: I don't know that I can answer that. Its use as a rectifier is in the hands of one party and I don't have very much definite information. I am not well acquainted with your use of the term "volt-ampere characteristic curve."

MR. FIELD: By "volt-ampere characteristic curve" I mean the record of the voltage impressed across a cell of tantalum electrodes, with a suitable electrolyte, such as an acetate, a borate, or the like, and the amperes resulting therefrom. This will give one point on the curve, and as the voltage is increased in steps, the amperes will increase up to a point where the flow of current for a given voltage

increases very rapidly. This so-called critical voltage or "knee" of the curve varies between 300 and 360 volts for aluminum and measures the adaptability of the electrode material to rectification and lightning arrester work. It should be noted that this volt-ampere curve is recorded under constant conditions, after the cessation of the first rush of current which builds up the film. This first rush of current is of a large magnitude, being limited only by the internal resistance of the electrolyte, and very rapidly diminishes to a constant value as the film builds up.

MR. BALKE: We do not know because we have not run experiments above 75 volts. Up to 75 volts, as far as we can make measurements on the back leakage, the amount is so small that it is very difficult to measure it at all. It is not over one mili-ampere for 75 volts.

MR. FIELD: The breakdown voltage for aluminum is about 350. Have you any figures of the breakdown voltage of tantalum?

MR. BALKE: No; we have not used voltage that high in our experiments.

MR. ALBERT E. MARSHALL: There is one question I should like to ask Mr. Balke, whether he has any information as to the action of phosphoric acid on tantalum?

MR. BALKE: I believe that tantalum is not acted on by this acid.

MAGNESIUM OXY-CHLORIDES, THEIR PROPERTIES AND USES IN THE CONSTRUCTION FIELD

By MAX Y. SEATON

Read at the Richmond Meeting, December 6, 1922

In 1867 a Frenchman named Sorel, after investigating the reaction between zinc oxide and strong solutions of zinc chloride, extended his studies to other metallic oxide-metallic chloride combinations. The behavior of magnesium oxide-magnesium chloride mixes was of particular interest, and he investigated their properties at some length. The magnesium oxy-chloride formed from such a mixture proved to have exceedingly valuable cementing powers. It is this material which is the basis of the present magnesium oxy-chloride or Sorel cement industry.

Because of the ability of these oxy-chlorides to bind woody fibers into a firm, compact mass, giving a structural material of unusual resilience and yet good hardness, Sorel cement was first used in the preparation of composition floors, for in this field it was soon seen to fill a need not met by any other structural material. Very early, too, an effort was made to use Sorel cements in the preparation of exterior wall coatings or stuccos, for the lime stuccos commonly in use at that time left much to be desired as regards both cost and structural properties. A little later the magnesium oxy-chlorides were used for the preparation of artificial building stone, artificial marble, tile, and similar shapes.

Although a certain amount of success was obtained in most of the lines tried, yet numerous failures continued to occur, frequently from apparently inexplicable causes. It is fairly easy to see how such a condition came to exist. Oxy-chlorides were ordinarily used by artisans who, although possessing excellent mechanical ability, had no real knowledge of the behavior of cementing materials as a class, which, as a matter of fact, require fundamentally different treatment. It has only been within the past ten years that sound data on the characteristic behavior of oxy-chlorides has become available, that

their seeming eccentricities have been explained, and that rapid progress has been made in the development of the industry.

The growth of the industry to its present importance can be directly traced to the fact that magnesium oxy-chlorides have certain properties as a binding material not shared by any other cementing medium in common use. In proper mixes they attain high strength at a very early age, and this with free exposure to the air, letting surface evaporation go on as it will. This is obviously in marked distinction to the behavior of either Portland cement, lime, or gypsum products, all of which must be guarded from premature loss of water before complete hardening has occurred. The oxy-chlorides, too, show a volume change, due either to setting reactions or to temperature changes, lower than that exhibited by any other common structural material. As has been previously noted, also, the oxy-chlorides are unique in their ability to bind woody or fibrous aggregates to a product of high strength, thus making possible the development of a mass of distinctive characteristics. In the present-day use of oxy-chlorides it will be found that the fields invaded by these products are those which call for one or another of the properties indicated, in higher degree than that exhibited by competitive products.

Although much time has passed since the discovery of the reaction between magnesium oxide and magnesium chloride solutions, the mechanism of the reaction and the constitution of the finished product is still the subject of considerable dispute. Space can not be given to tracing the progress of the controversy on constitution or to the conflicting views of different observers. There is little question but that the views of both sides, one of which contends for a definite chemical compound and the other for a colloidal or solid solution, are in part correct. Recent physical chemical research indicates that the binding materials existing in the average commercial product are in part made up of a definite chemical compound, $3MgO \cdot MgCl_2 \cdot 10H_2O$, and in part of a solid solution of magnesium chloride in magnesium oxide or hydrate. The relative proportion of these two compounds may differ considerably in different cements. In all cases, however, the solid solution probably amounts to at least half of the total binder, and its properties strongly influence the characteristics of the cement.

The chemist has long known that the magnesium oxy-chlorides were decomposed by water, with the formation of magnesium chloride

in solution and the precipitation of magnesium hydrate. By many this fact has been considered to mean that oxy-chloride cements could never withstand the action of water without serious loss in cementing properties and consequent deterioration in structural value of any material in which oxy-chlorides were used. Such reasoning is fallacious. Certain forms of magnesium hydrate closely resemble the natural mineral brucite (magnesium hydroxide) in properties, having high strength and excellent binding power. Fortunately, it is to these forms of hydrate that oxy-chlorides revert when such oxy-chlorides are of proper constitution and are weathered or wet in normal fashion. The recollection that the calcium hydrate in lime mortars is slowly transformed to calcium carbonate on aging should be sufficient to lay at rest the fear that a change in the composition of a cementing material need necessarily result in structural unsoundness.

The solid solution which always constitutes a major part of magnesium oxy-chloride cements contains a considerable amount of water. Its water content varies according to its environment, being lower as temperature rises and humidity of the air drops, and higher as the reverse changes take place. As water content is reduced slight shrinkage of the oxy-chloride results, while slight expansion follows increase in water content. This is exceedingly fortunate, for it tends to counteract the normal volume changes which occur through temperature change. That is, the usual expansion with rise in temperature is, with the oxy-chlorides, counteracted, at least in part, by the shrinkage caused through loss in water of the basic binding material. It is particularly for this reason that the oxy-chlorides have the name of being remarkably free from expansion or contraction movements.

Of the raw materials employed in the oxy-chloride cement industry, magnesium oxide stands first in importance. In Sorel's time magnesium oxides prepared from magnesium-carrying natural brines were employed. This type of material is used but very infrequently in the oxy-chloride industry to-day, although it holds some possibilities for the future, where special oxy-chloride cements are in question. Essentially all of the magnesium oxide used by the industry at present is obtained through the calcination of natural magnesium carbonate or magnesite, and appears on the market under the name of plastic calcined magnesite.

There are large deposits of magnesite in Greece and in Austria,

and it was from these sources that the expanding oxy-chloride industry on the European continent obtained its magnesium oxide supply. In fact, up to 1914 all but a very small fraction of the magnesium oxide used by the industry in the United States was obtained from these sources. The war abruptly closed this source of supply, and it became necessary to develop magnesium oxide production in this country. In 1914 the oxy-chloride industry was by no means as strong as it is to-day, and it is possible that it might have failed in its attempt to secure domestic production but for the emergency which the shutting off of magnesite imports caused in the steel industry. It was, first of all, the demands for magnesite for steel making which led to the rapid development of the magnesite deposits of California, and later to the exploitation of the Washington deposits. From these sources plastic calcined magnesite, sometimes of questionable grade, began to reach the market. Later, as demand for refractory magnesite was reduced and importation was again established, our domestic deposits were developed into producers of plastic calcined magnesite alone, little or no dead burned magnesite having been produced in this country for two years past.

Consumers of plastic calcined magnesite throughout the early development of the industry experienced grave difficulty in purchasing a product of satisfactory cement-making properties. Plastic calcined magnesite was sold wholly on analytical specifications, the content of magnesium oxide, of ignition loss, and of lime ordinarily being kept within moderately close limits. It developed that magnesium oxides of identical chemical analysis did not necessarily have comparable cement-making value. At the joint instigation of the world's largest oxy-chloride producer and of the largest magnesium chloride producer in the United States investigations were undertaken which ended in showing the causes for the discrepancies previously noted, for the first time establishing the industry on a substantial basis.

The gypsum and the Portland cement industries have definitely established that the physical character and cement-making value of their products can not be specified in terms of chemical analysis. The lime industry has recently found the same facts to hold true for its particular field. A parallel case exists in plastic calcined magnesite. Laboratory investigators have long known that the reactivity of magnesium oxide was largely a function of the time-temperature history of its calcination. At one extreme stands the active oxide

first formed when carbon dioxide is just barely removed from the natural carbonate, while at the other extreme artificial periclase is found. This is still magnesium oxide, but shows no ability to react with magnesium chloride solutions or to become hydrated in contact with water. Neither of these products is satisfactory when used in the preparation of oxy-chloride or Sorel cements. The material desired lies somewhere between these two extremes. Unfortunately, there are as yet no methods which will *rapidly* identify the particular oxide which the oxy-chloride industry needs. Recourse must be had to the preparation of oxy-chloride cements and the examination of their physical properties. In other words, physical tests have practically wholly replaced the chemical tests once relied on, and it is through such physical tests that all production of magnesite should be guided.

Magnesite occurs in veins or nodules in serpentine rock in widely separated districts in California, and associated with dolomitic deposits in northeastern Washington. The Washington deposits are high in iron and particularly adapted to the production of refractory material. California deposits are in many instances almost iron-free, and burn to a product of such color that it can be employed in all branches of the oxy-chloride cement industry.

Formerly all plastic calcined magnesite was prepared in stack or upright kilns of the type of the familiar vertical lime kiln, and such kilns still persist in some California operations, although their product can never approach in quality the material obtained from other types of furnaces. If a magnesium oxide of high quality is to be prepared, time and temperature of calcination must be held within narrow limits. This is obviously impossible in the burning of lump ore in a stack kiln, where to insure heat penetration and decarbonization to the center of the lump so much heat must be supplied that the outer material is seriously over-burned. For production of high quality material the ore must be sized within quite narrow limits, and a kiln or furnace adapted for burning such fine ore employed. Up to this time, because of the temperature involved, only the rotary kiln has been in active use. The Wedge or Herresoff furnace may perhaps find a field in the treatment of the higher iron ores, which calcine at a low temperature, but it is doubtful whether they will withstand the temperatures involved in the treatment of the purer ores, which must be heated to approximately 1,100 degrees Centigrade.

In mining operations care must be taken to hold the analysis of the ore delivered to a calcining plant within quite narrow limits. This is the principal place in the magnesite calcining industry where chemical analysis is of vital importance. As calcium carbonate is fairly completely decomposed at the calcining temperatures employed, and as the resulting calcium oxide is exceedingly injurious to the oxychloride reaction,[1] lime content must be held at a low figure. Then, too, small amounts of certain substances, notably iron, and to a lesser extent alumina and silica, influence catalytically the reactions which occur during magnesite calcining. If they are present in quantity, calcining temperatures must be lowered materially to avoid overburning. These impurities are not injurious in the sense that lime is, but ore containing them must be kept separate from ore containing no such material and treated in individual fashion in order to yield a satisfactory product.

No particular comment is called for on the general operations of mining or of crushing the ore before calcination. In practice it is found that half-inch sizing is essential if the appearance of either over-burned or under-burned material in the finished product is to be avoided. Kiln practice, however, is essentially different from that common in either the cement or the lime industries, although it is conceivable that the lime industry will some day employ the methods used in the preparation of calcined magnesite. In the operation of a rotary kiln for magnesite production not only must the maximum temperature in the kiln be carefully regulated, but a temperature closely approaching the maximum must be maintained over a zone of considerable length. In normal practice the carbon dioxide is expelled from the magnesite at a temperature much below that necessary for the development of the particular type of magnesium oxide which is desired. Gas is fairly well liberated, in other words, before the ore enters the zone in the kiln in which definite temperature is maintained. It is the length of this zone, its temperature, and the rate of passage of magnesite down the kiln which determine the character of the calcined product. Space is too limited to discuss here the special features of burner design and of flame control which are necessary to obtain the necessary kiln conditions, or of the methods of pyrometry required to follow and control them. It is sufficient to say that the major problems in connection with the operation have been solved,

[1] Seaton, Hill, and Stewart. *Chem. Met. Eng.*, 25, 270–4 (1921).

and that the quality of magnesite produced in a rotary kiln is consistently higher than that of similar material produced in any other type of furnace operating commercially.

The calcined magnesite must be ground to a product somewhat finer than ordinary Portland cement. For this grinding the use of ball or tube mills is not permissible, because of the packing of the material on the sides of such a mill. The ring-roll mill using air separation or the burrstone mill give excellent products. For this particular grinding problem the old-fashioned burr mill, which has fallen into disrepute in many industries, is particularly adapted and gives a material difficult to equal by any other type of mill.

The finished plastic calcined magnesite is a fine powder, about 85 per cent of which passes a 200-mesh screen. It varies in color from white through creams to dark browns or even chocolates. The darker colored product may have intrinsically the same cement-making properties as the lighter materials, giving only a cement of darker color, and consequently limited to use to those cases where light color in the finished product is no object. The cream-colored magnesite may give even a whiter cement than the pure white magnesite.

The quality of plastic calcined magnesite is now determined by all progressive operators strictly through determination of physical properties of the cement which it gives when mixed with magnesium chloride and suitable aggregates. Chemical analysis is still made, but largely as a matter of interest, for its bearing on the cement-making properties of the product is very slight.

Although the domestic reserves of magnesite are sufficient to supply the industry for many years to come, it has been recognized that the growing demands of the industry will eventually deplete these deposits, and another source of magnesium oxide may be required. The most promising possibility lies in the extensive and widespread dolomite deposits of the country. Several writers[2] have indicated methods for making such dolomites available for the oxy-chloride industry. These methods involve either the burning of the dolomites at a low temperature in the attempt to prevent the decomposition of calcium carbonate, the leaching out of the lime from a burned dolomite with water, or the burning of a dolomite in an atmosphere high in carbon dioxide to repress the dissociation of the calcium carbonate.

[2] Clark, British Pat. No. 1720, 1881. Schurecht, *J. Am. Ceramic Soc.* 4, 558 (1921). Bole and Shaw, *J. Am. Ceramic Soc.*, 5, 817 (1922).

All of these methods have been tried in the laboratory and even on small plant scale. The success of any or all of them in commercial practice is as yet problematical.

Magnesium chloride is also an essential raw material for the industry. The potash deposits in the Stassfurt region in Germany contain, of course, enormous quantities of magnesium chloride, which in more or less impure form is a waste product from potash plants. German magnesium chloride was for many years the standard of the industry in the United States, but, particularly since the war, domestic production has taken the place of first importance.

Two main sources supply all domestic magnesium chloride. One is the bitterns remaining after evaporation of sea water or of the brines from the Salduro marshes in the Great Salt Lake district. These bitterns are concentrated by solar evaporation, and an impure magnesium chloride solution, containing also magnesium sulphate and sodium and potassium salts, is obtained. This is further concentrated until the majority of the sodium and potassium salts and all but about 3 per cent or 4 per cent of the sulphates are removed. The material is finally marketed either as concentrated solution, in the form of loose crystals wet with mother liquor, or as fused solid. The Salt Lake district produces magnesium chloride only in connection with potash production, and as the potash plants there have been inoperative for some time past the district has ceased to be a magnesium chloride producer. At least four different operators on the Pacific Coast, however, send liquid or crystal magnesium chloride to the Western market.

The most important domestic source of magnesium chloride is found in the salt brines of Michigan, which are worked primarily for bromine. These brines contain also large quantities of calcium chloride, so that a simple separation of magnesium chloride by evaporation is not possible. Methods have been developed, however, for making the chemical separation from calcium within reasonable cost limits and so completely that the magnesium chloride produced ranks higher in purity than that obtainable from any other source. It appears on the market as fused solid or as flake or granular material, which latter is a distinct advantage from the standpoint of handling in the field.

Quality of magnesium chloride can be definitely specified through specification of limits of impurities and of content of anhydrous mag-

nesium chloride. A chemical analysis gives all the information desired.

In actual preparation of oxy-chloride cements a more or less dilute solution of magnesium chloride is employed. Strength of this solution is observed by determination of its specific gravity with a hydrometer, the Beaumé scale being universally employed. The preparation of this solution is left either in the hands of the worker handling the finished cement or in the hands of a supplier who furnishes it to the worker in liquid form adjusted to correct strength.

The remaining raw materials of interest to the industry may be classed under the general head of aggregates, and require very close attention by operators producing oxy-chloride cements. For a number of reasons the practice of assembling mixes at the point where they are to be applied—that is, adding sand and other aggregates to the magnesium oxide in the field—is not permissible. In the first place, only dry aggregates can be used, as the oxy-chloride cements are very sensitive to variation in the strength of magnesium chloride employed in their preparation. If wet aggregates are used, it is impossible to make proper adjustment for the varying amount of water thus introduced. Furthermore, special knowledge is required for the choice of satisfactory aggregates. Not only are more materials needed than are employed in concrete or gypsum plaster practice, where sand or sand and stone only are required, but the requirements for a satisfactory sand are quite different from those which hold in the preparation of high quality concrete. If sand only were needed in oxy-chloride cements, education or the insistence on special screening methods might solve the difficulty. All commercial products, however, contain a fine aggregate, such as silex or marble dust, and almost invariably a fibrous material such as asbestos. These materials, of standardized quality, are not available locally at the points where such cements are used. Even more vital is the fact that the principles of oxy-chloride mix formulation are perhaps more complicated than those which hold for concretes. Mix balance is not improved by adding more magnesite as a factor of safety to take care of inferior aggregates, as can be done with Portland cement in concrete work. Instead, the quality of an oxy-chloride mix is deteriorated if either too much or too little magnesium oxide is employed, and for best results the quantity of oxide used must be carefully regulated to the characteristics of the other materials used in the mix.

For this reason factory prepared mixes are standard in the oxy-chloride industry, and despite the disadvantages of such mixes in somewhat higher cost for transportation there is little likelihood of the use of field prepared mixes gaining in favor.

Little further comment is required on the various classes of aggregates employed. The sands used must be clean and free from loam, as is the case in concrete practice, but they should preferably be decidedly finer than a good concrete sand. The fine aggregate must be neither too fine nor too coarse, a material largely passing a 100-mesh screen, but showing not over 65 per cent, passing a 200-mesh being preferable. It may be either ground silica, known commercially as silex, or ground limestone or marble, provided this latter rock is hard, so that the individual particles of fine aggregate prepared from it show good strength. The fibrous materials which are almost invariably used may be either a short-fibered asbestos or wood sawdusts or flours of carefully regulated properties. In special cases other materials are also employed in oxy-chloride mixes, such as clays, to give greater plasticity and ease of working under the trowel; talcs, also for their trowelling effect; or colors, particularly in the various composition floors which employ oxy-chlorides as a binder.

The most fundamental principle involved in the formulation of suitable oxy-chloride mixes may be described as the "thin glue joint" principle. It is common knowledge that in gluing two pieces of wood best mechanical properties are obtained when the glue film between the two wood surfaces is of minimum thickness. Exactly the same principle holds for oxy-chloride mixes. The magnesium oxide-magnesium chloride mix which eventually gives an oxy-chloride of some indefinite composition should be considered as a mineral glue which will function to best advantage only when it is present as thin films between closely packed particles of aggregate. Because the reaction between magnesium oxide and chloride is almost totally complete, without the surface reaction effect which exists between Portland cement particles and water, it is necessary to supply fine aggregate partially to fill the voids between the coarser sand particles. If this is not done, so large a volume of oxy-chloride cement appears between sand grains that the thin glue joint principle is violated and weakness results. It is obvious that in following out this principle a mix of high density is unavoidably obtained.

Finally, oxy-chloride cements are used in by far the majority of

cases by workmen of only ordinary skill, who in most instances handle the plastic cement with trowels or similar tools. It is obvious that such a worker will obtain best mechanical results if the mix is easy to handle and can be applied with only normal effort. For this reason attention is given by oxy-chloride manufacturers to the production of high plasticity in their finished materials. This is usually done through the addition of asbestos or a related fibrous material. Fortunately, as will be later shown, such an addition is permissible here, and the change in ratio of liquid to solid resulting is not detrimental, as it is in Portland cement practice.

Of vital importance, too, in the preparation of oxy-chloride cements is the question of the strength of the magnesium chloride solution employed. General experience has indicated that a solution of a gravity of 22° Beaumé gives best results, and that if this strength is greatly departed from trouble will result.

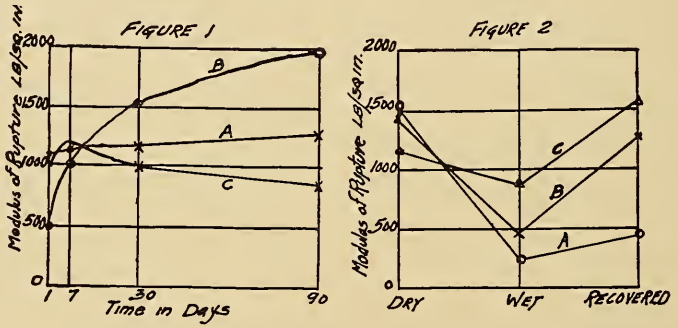
The properties of oxy-chloride cements which are of interest from an engineering standpoint can, of course, be investigated only through the application of sound physical testing methods. A previous paper by the writer [3] has indicated some of the tests which are advantageous, and they need not be further elaborated on here. A distinctive feature of such test work is the employment of the cross-bending test made on thin bars of the oxy-chloride cement, instead of the more common tensile strength of briquettes or compression tests of cubes or cylinders. This procedure has been adopted because the conditions of aging of such flat test pieces parallel quite closely conditions existing in field practice, where the major uses of oxy-chloride products involve their placing in thin layers with free exposure to the air.

Oxy-chloride cements are particularly notable from an engineering standpoint because of their rapid attainment of high strengths. The rate at which such strength is attained and the subsequent behavior of the cement after maximum strength has been reached are dependent in part on mix constitution. Given a mix of proper balance, however, these factors are even more directly related to the properties of the magnesium oxide employed, which, as has been earlier indicated, may be varied by varying calcining conditions. Fig. 1, for example, shows the behavior of three different oxy-chloride cements, using in each case the standard testing mix, containing one part of calcined magnesite, two of silex, and five of standard sand, but varying the mag-

[3] *A. S. T. M. Proc.*, 21, 1039–49 (1921).

nesite used. Curve *A* indicates the more or less familiar behavior of the oxy-chlorides in which some 80 per cent of final strength is developed in the first twenty-four hours. Curve *B* indicates an even more desirable type of cement for many purposes, the strength gain being progressive and final strength very high. An improperly burned magnesite, such as is sometimes encountered, may give the type of strength curve shown at *C*. The retrogression in strength indicated here has been reported as characteristic of oxy-chloride cements by many investigators. It does not occur, however, in a properly balanced mix when a normal magnesite is employed.

The question of the behavior of oxy-chlorides in contact with water has been previously mentioned. This again is a property



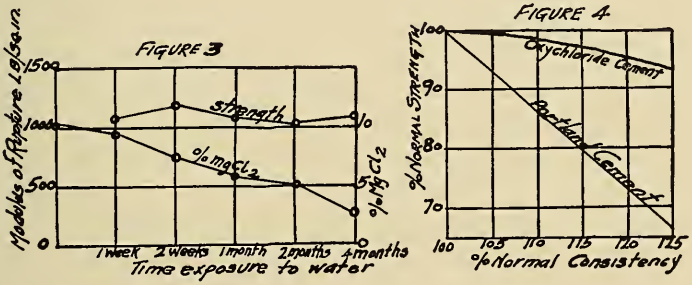
Curves indicating the Behavior of Oxy-chloride Cement.

which is largely influenced by the character of the magnesite employed. Fig. 2 gives results on three typical magnesites, using for the tests the methods described in the paper [4] earlier mentioned. The cement indicated at *A*, although it has very high initial strength, does not withstand water well and could not be considered of high quality. *B* is a marked improvement, but its wet strength is still too low. *C*, although it does not have nearly as high strength before water treatment as the other two materials, yet is markedly superior to both of them in its ability to withstand dampness, for it shows but a moderate reduction in strength on wetting and after redrying has even a higher strength than it possessed before water treatment.

In this connection it should be noted that a fundamental feature of the ability of oxy-chlorides to withstand water is the fact that

[4] Seaton, *A. S. T. M. Proc.*, loc. cit.

means must be provided to insure proper drainage of water from their surfaces, to prevent the collection of stagnant water on them, or their immersion in a small volume of water for lengthy periods. Under these latter conditions the water in which they are immersed, or which lies on their surfaces, soon becomes impregnated with magnesium chloride. Magnesium chloride solutions deteriorate oxy-chloride cements rapidly. When proper drainage is supplied, or when the water volume is large or in continual circulation, chloride is removed just as in the former case, but it does not accumulate and act on the oxy-chloride, and no failure results. The behavior under normal exposure to water of a properly prepared oxy-chloride is indicated in Fig. 3, which shows the comparative change in strength and change in chloride percentage of a mix subject continuously to water spray.



Curves indicating the Behavior of Oxy-chloride Cement.

Effect of strength of chloride and of change in mix composition have also been shown in an earlier paper.[5] One other feature of the behavior of oxy-chloride cements may bear mention here—that is, their ability to give high strength even when exceedingly wet mixes are employed. The Portland cement industry has been emphasizing strongly of late the fact that cement-water ratio is an all-important factor in determining concrete strength, and that if wet mixes are used strength is rapidly lowered. Although indications of the same effect are seen in the oxy-chlorides, the actual quantitative influence is much less. Comparative curves for a Portland cement mortar and for an oxy-chloride cement are given in Fig. 4, which brings out in quite striking fashion the reason for the observed fact that oxy-

[5] Seaton, loc. cit.

chloride mortars can be prepared of quite a wide range of workability and still show little change in final properties.

Because of the distinctive ability of the oxy-chloride cements to form satisfactorily and to reach high strength with free exposure to the air, such products have been most widely used in those instances which require the application of a plastic coating in thin layers. The structural fields in which such conditions must be met are so broad that as yet little attempt has been made to introduce oxy-chlorides into other fields in which they may also be of value. With the stabilization of the industry and the availability of magnesite of uniform quality an assured fact, engineers are exhibiting more and more interest in this type of cementing material, and are applying it to special problems.

The normal oxy-chloride or composition floors are of interest to the chemical engineer chiefly through their uses in buildings intended for light manufacturing, such as the preparation of fine chemicals, or as floors in laboratories. In such locations they are dustless, very resistant to abrasion, comparatively warm and soft under foot, and have the advantages of a hardwood floor with few of the disadvantages of such a material. The fact that they are considered standard by many architects specializing in hospital design is indication enough of their sanitary qualities, which for the uses indicated is also an important factor.

The majority of current oxy-chloride practice is concerned with the preparation of exterior stuccos using these products as binders. Such stuccos have as yet played little, if any, part in factory construction. It should be realized, however, that because of their enormous strength and freedom from cracking, and because of their rapid aging, they offer marked possibilities for the construction of light buildings which must be erected with a maximum of speed and which are yet subject to such corrosive influences as would rapidly destroy sheet iron. Oxy-chloride stuccos can be applied either on wood or on zinc lath. When they are thus applied to ordinary wood studding, they make a building of high fire resistance, because of their non-combustible nature and also because of the fireproofing effect on all exposed wood of the magnesium chloride used.

The oxy-chloride interior coatings or plasters have recently found a distinct field in the treatment of the interior of buildings intended for the manufacture of fine chemicals, pharmaceuticals, etc., where

absolute sanitation and cleanliness are essential. Such interior plasters, being waterproof and crack-free to an extent never obtainable with gypsum or lime products, lend themselves particularly well to circumstances where a plaster coating must meet heavy duty requirements.

Of great interest also is the use of oxy-chlorides for special mold work in the preparation of castings. Not only have they been employed for master patterns, but also for emergency work in which a pattern of a broken casting is desired. A thin oxy-chloride mix can be cast in a sand mold and will be firm enough to handle and true up inside of twenty-four hours, serving then as a pattern for a casting in metal. Oxy-chlorides have also been employed for cements in setting brick where great strength is required, for the lining of tanks to contain oils or fatty acids, for the construction of diaphragms, and many other miscellaneous uses.

A possible field for the use of oxy-chlorides in engineering practice, which has yet been but briefly investigated, is their employment in the construction of built-up structural members to replace concrete where exceedingly light weight is desirable. Their strength is so high, being several times that of the strongest concrete obtainable, and the possibility for use with them of light aggregates is so attractive, that it is very likely that this field will eventually prove one of the main outlets for the products of the industry.

It is obvious from the discussion above that the oxy-chloride industry is yet in its infancy. Although the oxy-chloride reaction itself has been known for many years, the thorough study of the oxy-chlorides which has resulted in a fairly complete knowledge of their behavior is a matter of the very recent past. They offer, however, a plastic material of unique properties which is certain to find a sphere of usefulness not only in the stucco and flooring fields, in which they are already well established, but for many other structural purposes as well. It is confidently expected that the next few years will show growth of the industry in many directions which can not even be anticipated at this time.

GLASS RINGS—A NEW FILLING MATERIAL FOR TOWERS

By F. C. ZEISBERG

Read at the Richmond Meeting, December 6, 1922

In a recent article[1] entitled "The Efficiency and Capacity of Fractionating Columns," W. A. Peters, Jr., describes experiments on fractionating columns packed with various materials; among others, hollow cylinders. It was shown that hollow cylinders have so much greater capacity per square foot of gross cross-sectional area than solid filling material of approximately the same dimensions that it seemed worth while pursuing the matter to see whether such hollow cylinders in small sizes could not be produced commercially. The desirability of the smaller sizes lies in the fact that the separating efficiency in a packed fractionating column increases almost directly as the size decreases.

So-called Raschig rings of earthenware and metal have been used for some time, but of larger dimensions than Mr. Peters' experiments indicated to be desirable. Thus the General Ceramics Co. makes unglazed earthenware rings, 1 x 1 in. with 1/8 in. walls, of two different types. One of these is a plain, open-ended, hollow cylinder, the other a similar cylinder with four notches at each end. Maurice A. Knight makes both glazed and unglazed cylinders in four sizes: 5/8 in. with 1/8 in. walls, 3/4 in. with 3/16 in. walls, 1 in. with 3/16 in. walls, and 1 1/4 in. with 1/4 in. walls.

In Germany both porcelain and metal rings have been in use for some time, but so far as we have been able to learn, the smallest size used up until now is 15 x 15 mm., with 2 mm. walls in the case of porcelain and 0.5 mm. walls in the case of metal.

In England, Lessing[2] has attempted to improve the metal ring by adding a single central partition. This increases the surface of a given ring about 32 per cent. The Hydronyl Syndicate of London is marketing Lessing's ring in several sizes and in a variety of metals,

[1] *J. Ind. Eng. Chem.*, 14, 476-9 (1922).

[2] *J. Soc. Chem. Ind.*, 40, 115-9T (1921).

such as copper, iron, aluminum, and nickel. The cost of these rings is rather high.

It is probably true that the commercial limit has been reached with respect to further decrease in size of earthenware rings. Not only does the effective free space rapidly decrease as the ring size decreases, owing to the necessity of keeping the walls comparatively thick, but the cost of handling the rings in the drying and burning operations rapidly increases also. Furthermore, for some purposes, as, for example, handling hot sulphuric or nitric acids, the earthenware rings are not entirely suitable, tending to disintegrate.

While metal rings can easily be made of any desired size, no matter how small, by the use of automatic machinery, here the increase in surface per cubic foot of rings as the size decreases can in some instances work harmfully rather than otherwise. For example, in the distillation of acetic acid through a copper column filled with copper rings, the action of the acid on the copper is comparatively slight, measured in inches penetration per month; but when the enormous area exposed by the smaller size rings (252 sq.ft. per cu.ft. for ¼ in. Lessing rings) is taken into consideration, the total amount of copper dissolved is no insignificant factor. This holds, of course, wherever the metal composing the ring is attacked, however slightly, by the vapors or liquids coming in contact with it, and this condition obtains in a surprisingly large number of works-scale cases.

It seemed to us, therefore, that neither metal nor earthenware promised to be the ideal material of which to fabricate small rings. In looking about for such a material, glass naturally suggested itself. Glass is a fairly cheap material, is inert to a large variety of chemicals, possesses the necessary strength, is a poor conductor of heat (which is an important consideration in a column where reactions occur having a marked temperature gradient), and is readily cleaned.

Considerable effort has been spent on methods of manufacturing these glass rings, and this has been successful to the point that the chemical department of the du Pont company is now in a position to market small glass rings at prices which make them attractive for a number of operations, notably for the filling of small distilling columns. The rings can be made in a large range of sizes. For each operation, however, there is an optimum size, indications being that for all-around purposes ring No. 11 is about the best. Table I shows the properties of the various size rings.

TABLE I

Properties of Glass Filling Rings

Chemical Department, E. I. du Pont de Nemours & Co.

Size*	4	5	6	7	8	9	10	11	12
No. per cu. ft.	369,000	189,000	109,300	68,800	46,100	32,400	23,600	17,750	13,650
Wt. per cu. ft., lb.	52.0	49.1	46.2	43.4	40.5	37.7	34.8	32.0	29.1
Sq. ft. per cu. ft.	415	332	274	233	203	178	160	144	130
Per cent. free space	66	68	69	71	73	75	77	79	81
Wall thickness, mm.	0.58	0.63	0.68	0.73	0.78	0.83	0.87	0.92	0.97
Resistance, inches H_2O	9.4	6.7	5.0	3.8	3.0	2.4	1.9	1.55	1.27
Price per cu. ft.	$115.00	$65.00	$42.00	$31.00	$24.00	$20.00	$17.00	$15.00	$13.00

* The size number of the rings is simply the outside diameter in millimeters.

It should be emphasized that the weight, wall thickness, free space, and surface shown in the table are only approximate. The wall thickness for a given size can be varied considerably, and with it all the other properties vary as a matter of course. The properties given, however, are for what appears the best proportioned ring.

The resistance shown is the pressure necessary to force 1,000 lb. air per hour, at 20 deg. C. and 760 mm., through a bed of rings having a cross-sectional area of 1 sq.ft. and a depth of 1 ft. The figures were calculated by the formula given in F. C. Blake's paper, "Resistance of Packing to Fluid Flow," and are probably accurate to within less than 10 per cent.

The prices given are tentative. They are for quantities of 50 cu.ft. or more and are f.o.b. Wilmington, Del. Prices on small quantities of the smaller rings for laboratory use will, of course, be considerably higher.

The du Pont company has these rings in use in several distilling operations. For example, a 9-in. column, filled with 13 ft. of No. 9 rings, is producing 2,000 lb. per day of 90 per cent (by weight) alcohol from a 60 per cent feed alcohol, with a heat flow up the column of 220,000 B.t.u. per sq.ft. of cross-sectional area per hour. The performance is equivalent to that of a thirty-five-plate column, and has been satisfactory from the first.

In a second operation a 4-in. column, packed with 11 ft. of No. 11 rings, is used in stripping a 28 per cent ammonia liquor. The feed rate is 90 lb. of liquor per hour, with a heat flow of 395,000 B.t.u. per sq.ft. of cross-sectional area per hour. A vapor at approximately room temperature is delivered from the top of the column, while the hot water running from the base is NH_3-free. In this case only 6 ft. of the packed space is really functioning, equivalent to about sixteen plates, the remaining 5 ft. being used as insurance.

To illustrate the readiness with which these glass rings can be cleaned, this NH_3 column stopped up several weeks after being put in operation, and when it was opened the rings were found stuck together with a dark brown deposit which was found to be iron salt. The rings were simply removed, treated with commercial hydrochloric acid, which readily dissolved the deposit, washed with water, and replaced in the column.

In conclusion, it should be stated that the du Pont company has made what is felt to be only a very limited application of these rings

to works-scale operations. Those applications susceptible to patent protection, however, as well as the phases of ring manufacture which can be covered, have been taken care of.

Discussion

Mr. Wadsworth: I want to ask about the size of these rings. I don't know that you gave the various sizes of rings that you have made.

Mr. Zeisberg: The sizes are given on the sheets that were passed around. The size is simply the outside diameter in millimeters.

Mr. Weiss: In this type column installation, is it necessary to have a reflux condenser or back flow?

Mr. Zeisberg: Yes; this column is no different from any ordinary distilling column at all. Of course, the most efficient separation in the operation of a column demands a high reflux ratio, and also demands that there be as little heat lost from the column as possible. The old practice of operating a column with bare walls in order that heat may be lost from the column itself, so that the column itself may act as a partial reflux condenser, is very inefficient.

Mr. Weiss: What proportion of back flow to forward flow can you get without flooding a column of this type? That is one of the limitations of the bell column; that you can not always get the ratio of back flow which you want. Sometimes it is desirable to have a back flow 10 or 15 times the forward flow. Have you determined the maximum ratio?

Mr. Zeisberg: I think you will find the detailed answers to all those questions in this article by Mr. Peters to which I have referred, which came out in the "Journal of Industrial and Engineering Chemistry" early in the year. The factor that determines the point at which the column loads is the amount of vapor passing upwards. We have found by reducing the vapor to B.t.u. per square foot per hour, the column always loads at approximately the same B.t.u. rate, and that is the reason I included these B.t.u. figures in my paper.

Mr. H. O. Chute: The subject of fractional distillation is one that has interested me for some time, particularly in the separation of alcohol. It has been used on a very large industrial scale for many years. Several hundred years ago a Frenchman named Derosne invented an inverted bell tower consisting of chambers formed by a series of plates which are superimposed in a column, and through

which the ascending vapors must pass and thereby bubble through the descending liquid.

The universal experience of those who use distillation in large quantities, particularly for alcohol, and those who separate water from ammonia as in a gas works, proves that the inverted cup column is the most successful apparatus for any material which can be fractionally distilled. Copper as a material for construction lends itself, on account of its malleability, to the structure of the apparatus better than any other material and for that reason has been used very largely.

For the alkaline products, such as are obtained from gas works, iron is necessary. In many cases they can use wrought iron, which is a fairly workable material, particularly in our later-day methods of working, and in those places where cast iron is necessary that has been used.

With earthenware it might be difficult to construct the cup column, but for any material which can be worked in metal the experience of the world is that a Derosne column is the best fractionating apparatus. For instance, to-day they have column stills which will turn out 500 gallons per hour of 96.2 per cent alcohol, and for 24 hours it will not vary one-tenth of one per cent, and if the variation in boiling point was one-tenth of one degree Centigrade, you would get more than one-tenth of one per cent variation in the alcoholic purity.

Dr. James R. Withrow: It is interesting to see some one apply this laboratory idea industrially. I used to prefer the glass beads in what is called the Hempel distilling tube twenty years ago to the French device (Lebel-Henniger tubes) which we used in the laboratory up to that time, in which there are little side passages so that the liquor may be drawn off, from level to level past the platinum gauze baskets. I can remember well seeing some of the tubes used by the late Mr. Jayne, of the H. W. Jayne Chemical Company in Philadelphia, in sections up to 8 or 10 feet high, in which he made commercial distillations. It seems incomprehensible to us with our present large-scale operation to think of those things being done successfully in such glass apparatus. I have wondered why no one seems to have had the temerity to come out with these rings in columns until Mr. Zeisberg has done it.

President Howard: Mr. Zeisberg, have you anything to say in conclusion?

Mr. Zeisberg (closing): I should simply like to call attention to

the fact that the du Pont company does not claim that these glass rings are a substitute for every type of distilling apparatus. Every case has to stand on its own merits, the ability to stand the original cost and maintenance cost being the important considerations.

As Mr. Chute points out, copper is an ideal material from which to construct alcohol distilling columns, and I think it likely that the glass rings are in no danger of supplanting copper columns for larger operations; but in small stills the cost of the copper column decreases less rapidly than its capacity decreases, so that we soon reach a point where the cost of copper columns for small operations is excessive.

In the case of glass rings all we do is to take an iron pipe, dump a few cubic feet of glass rings in it, and we have a distilling column. That entails practically no maintenance cost, and in one case I mentioned we constructed that column (despite the fact that we charged the rings in at a higher price than shown on the sheet) for one-third of what a copper column of the same capacity would have cost.

PRESIDENT HOWARD: I regret that I must declare the discussion closed.

PYREX GLASS AS A MATERIAL FOR CHEMICAL PLANT CONSTRUCTION

By A. E. MARSHALL

Read at the Richmond Meeting, December 6, 1922

Anyone who has undertaken construction work on chemical plants, whether for the manufacture of mineral acids or less corrosive products, will admit that no available material gives satisfactory service under all conditions.

Materials in general use have specific advantages for specific work, and the chemical engineer utilizes a number of different materials in one piece of construction in order to develop maximum durability under varying conditions. Incidentally, durability is in many cases synonymous with resistance to corrosion.

Glass, because of its insolubility in acids, has always found uses in the chemical industry, but its limitations in the way of temperature resistance have restricted the field of application.

Limited Use of Ordinary Glass in Industry

Ordinary glass, if desired to withstand moderate temperature changes, has to be made into shapes with thin walls, and such shapes when thin enough to survive slight heat shocks are much too thin to stand up under ordinary plant usage, or in many cases to survive rough handling during erection.

The desire to make use of the non-corrosive properties of glass has led to its being tried out under a variety of plant operating conditions, but the inherent disadvantages of ordinary glasses so far outweigh the useful features that it is difficult to point to successful applications in plant-scale work except under special circumstances.

I remember making a survey some years ago of materials used in the construction of gas-conveying lines from hydrochloric acid pots and muffles. One plant at the time of my visit was using 15-in. slip joint glass pipes on the pot line. Very good results were being obtained because of the thorough cooling of the gas in its passage through the thin-walled pipes to the absorption tower. Later inquiries

indicated rather heavy breakage during the winter months, the cause being ascribed to leakage of melted snow through the roof and onto the pipes, or to the considerable difference in temperature between the atmosphere and the gas inside the pipes.

There was a purely local reason for the use of glass on this line. The chemical plant adjoined a glass factory, and the glass pipes were thin cylinders from the plate glass department.

When wire glass was introduced it seemed to offer decided possibilities to the chemical industry, and it was tried out for various uses without any great measure of success. I was very much interested in sulphuric acid concentrators at that time, and I substituted some wire glass plates for the acid-proof cover slabs on a cascade concentrator. The glass cracked in the course of a few hours and thereafter final collapse was merely dependent on the time required for the acid fume to attack the wire reinforcement.

Other engineers have endeavored to utilize glass in various ways, and where temperature resistance and mechanical strength have not been essential the material has proved satisfactory. I have in mind, as an instance, the glass-packed Gay-Lussac and absorption towers introduced in England about 1909 by Carmichael. These towers, usually of square section, are packed with annealed plate glass sheets, set on edge and spaced fairly closely. Each successive layer of packing is placed at right angles to the row below, thus giving excellent surface contact and good gas distribution.

Mention has been made of attempts to use, and the actual use of, ordinary glass in plant construction, because such attempts afford evidence of a desire on the part of the chemical industry to utilize the valuable non-corrosive properties of glass.

Industrial Possibilities of Pyrex Realized in Laboratory Ware

With the introduction of Pyrex as a laboratory material and as a domestic utility in the form of baking ware, the possibilities of using glass in plant construction assumed a more promising outlook. Chemical manufacturers tried out Pyrex baking ware for small-scale chemical operations, drawn Pyrex tubes were used in Hart nitric acid condensers, and many other minor uses were discovered for the standard shapes which were being produced for the laboratory or the home.

In December of last year the author suggested to the Corning

Glass Works the desirability of gathering together these sporadic developments and investigating the possibilities of producing a line of Pyrex products designed for the use of the chemical industry. The field appeared promising, and a decision was reached to establish an industrial Pyrex department, the author being retained as consulting engineer.

Before entering into a description of the present state of development, it is necessary to set forth the essential characteristics of Pyrex and the difference in its properties and ordinary glass.

What Pyrex Is

Pyrex is a low-expansion boro-silicate glass of simple chemical composition, containing no metals of the magnesia-lime-zinc group and no heavy metals.

A comparison of the linear expansion coefficients of Pyrex and a number of materials is given in Table I and, as will be seen, Pyrex has a smaller coefficient than porcelain, ordinary glass, or any of the usual metals.

The low coefficient of expansion introduces a marked distinction from ordinary glass whether of the lead or lime-soda type.

TABLE I

Linear Expansion Coefficients (Per Deg. C.)

Pyrex glass	0.0000032
Porcelain	0.0000036
Hard glass	0.0000077
Soft glass	0.0000085
Cast Iron	0.0000102
Wrought iron	0.0000119
Portland cement	0.0000120
Copper	0.0000167
Brass (66Cu-34Zn)	0.0000190
Zinc	0.0000258
Lead	0.0000276

The melting point of glass is not particularly valuable as an engineering consideration, as there is usually a fairly wide range between the initial softening point and final melting point. In the case of Pyrex, the softening point is about 800 deg. C., but the material will soften slightly, especially under pressure, if maintained for a long time above 600 deg. C.

In connection with the softening point, it is useful to remember that devitrification, which is a serious factor in the use of some materials, does not affect Pyrex in its working range.

Comparative Acid Resistance of Glasses

Acid resistance is not usually given much thought in the case of glass, the general assumption being that all glasses are equally resistant. Bulletin 107 of the Bureau of Standards gives considerable data on the acid-resisting qualities of Pyrex and other glasses, and is well worth study. Researches have also been conducted in the Corning laboratories on the resistance of Pyrex to perchloric, phosphoric, constant boiling hydrochloric, and concentrated sulphuric acids under a variety of conditions.

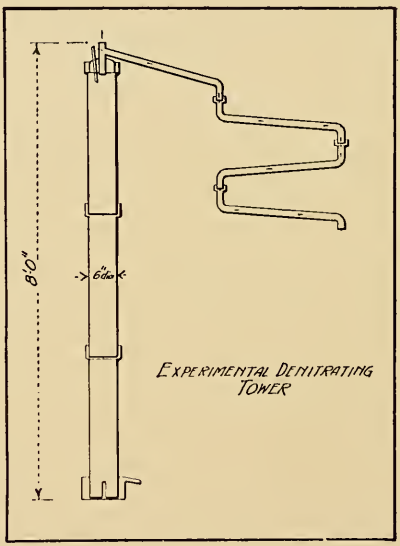


Fig. 1. Experimental Denitrating Tower, installed by the Du Pont Co.

The action of hydrochloric and sulphuric acid is very slight, constant boiling hydrochloric acid attacking Pyrex at a rate of 0.000006 gram per square centimeter per hour. Concentrated sulphuric acid in 4 hours at the fuming temperature shows an attack of 0.000002 gram per square centimeter per hour. Both figures relate to initial surface attack, as after the lapse of a few hours a state of practical stability is reached.

Work on the coefficient of heat transference is being carried out at Corning, but has not been completed. Preliminary results on the relative efficiencies of Pyrex, porcelain, and stoneware indicate Pyrex and porcelain as equal, whereas stoneware shows about one-half the Pyrex value.

It can be said that while Pyrex is superficially a glass, its physical characteristics justify consideration from the engineering standpoint as a special and distinct material adapted to a variety of industrial uses to which ordinary glass can not be applied.

The Development of Industrial Shapes

Proceeding from a consideration of useful properties to the development of definite industrial shapes, it is obvious that the upper limit of size is a factor of great importance. If the sizes had to be re-

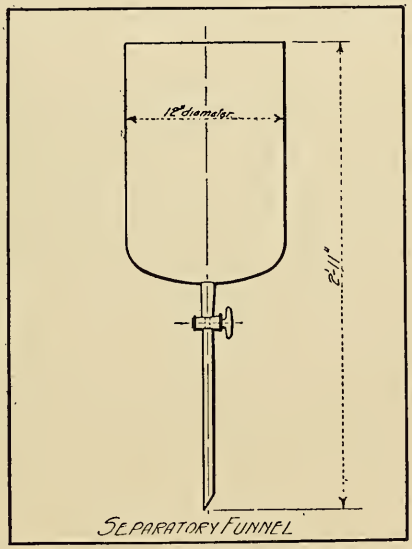


Fig. 2. One of the First Pieces of Pyrex Industrial Equipment

stricted below the usual standards in other materials, then the field of application would also be restricted. It was not practicable to pick out very large pieces and concentrate on them, for the reason that failure in manufacture might be caused by lack of dexterity in handling such large shapes. The history of most plant materials, stone-

ware, fused silica, high-silicon irons, etc., has been one of gradual enlargement of product. In the case of Pyrex the existing laboratory and domestic shapes could be used as a starting point and a stage selected which would represent useful commercial products without going out to sizes which would call for the introduction of new methods of handling.

The starting points selected were therefore an 18-in. evaporating dish, a 6-in. bore socket pipe 39 in. over all, and a cylindrical pot 12 in. in diameter by 20 in. high.

It was expected that difficulties would develop in the manufacturing process; but contrary to expectations, production was worked out with nothing more than the usual minor troubles.

With proof that manufacture was possible, it was then necessary to test out the product under working conditions. These tests were made on single pieces in various plants, and following satisfactory reports. distribution was started on a small scale.

Fig. 3. Pyrex Dish, 25 in. Diameter and 30 Liters Capacity

The application of these first available shapes brought along a demand for other forms of Pyrex equipment, and as a consequence new items have been added in the last few months, while others are approaching the production stage.

Reference is directed to the 72-liter capacity retorts, designed for distillation and reaction work, various sizes of pots up to 9-gal.

capacity, and large separatory funnels of 8-gal. capacity as articles now available.

Pyrex glass is also being produced in sheets 14 x 18 in., and it is expected that much larger sheets can be made if there is the necessary demand.

In addition to the above items, a 25-in. diameter dish of 30-liter capacity is about ready for distribution, 12-in. socket pipes will follow in a few weeks, and other shapes of equivalent size, such as a drier tray, cascade dishes, etc., will be put in production as soon as a demand is assured.

Incidentally the use of Pyrex in forms developed especially for the chemical industry has created interest in the possibilities of equipment made from Pyrex tubing. Condensing equipment made up of "S" bends, pipe lines with socket or butt joints, and many similar uses are becoming standardized.

A Pyrex Denitrating Tower

An interesting piece of Pyrex equipment was constructed recently for the du Pont Company. This was in the form of an experimental denitrating tower 6 in. in diameter by 8 ft. high. All parts, including distributor, inlet and outlet connections, were Pyrex. It is understood that the tower has given satisfactory service, despite rather strenuous conditions.

The use of Pyrex in actual plant work has developed some interesting sidelights, not only on applications, but on a phase of excessive cost, created by a lack of standardization. This point will be discussed later.

It had been expected by users that there would be a higher handling breakage with Pyrex dishes than with porcelain. Experience has been entirely to the contrary, and the reason apparently lies in the province of psychology. One plant, which is now completely equipped with Pyrex dishes, reports handling breakages as nil, and states that the men treat the dishes as glass, setting them down with care and so obviating breakages through dropping. It has been the experience of every user of Pyrex, irrespective of the shape of the article, that transparency creates care in handling. It is a natural assumption that an opaque object will withstand shocks and that a transparent one will not, so a transparent material which is at least equal to stoneware and porcelain in mechanical strength has a much

better chance to survive at the hands of a workman. Transparency has other advantages which are not psychological. The first and most important is that a transparent article can not have blowholes or other hidden flaws. Even strains can be detected by the use of a special polariscope, this being one of the routine tests to which every piece of Pyrex equipment is subjected in the Corning factory.

Next comes the question of cleanliness. Opaque equipment may or may not be clean, but transparent equipment always supplies its own positive answer on this point. Finally there is the feature of controlling reactions through direct observation.

Advantage of Rapid Process of Fabrication

Another interesting feature which has been brought forward by users is in relation to the process of manufacture. Pyrex is to a certain extent competitive with chemical stoneware. The process of making stoneware is quite lengthy, the time required being about 2 months. Breakage of a special piece of stoneware, provided there is no duplicate in the plant storeroom or at the stoneware manufacturer's works, means a long delay in starting up after the shutdown. Providing a mold exists for the piece in Pyrex, manufacture can be completed in 3 days as a minimum, although factory conditions might necessitate a delay of a few additional days on account of prior routing of work.

Touching on the phase of excess costs of construction materials, it seems very desirable to emphasize the lack of standardization in the chemical industry. Molds are costly, whether they are intended for stoneware, silica, Pyrex, or other materials. The manufacturer of the equipment has to charge up his mold cost to the user, and there seems to be too great a demand for "specials"—which may vary only $\frac{1}{8}$ in. from a stock mold. Some concerted effort to standardize shapes would cheapen the products, and, of equal importance, would enable producers to carry representative stocks. A striking example of the lack of standardization is shown by the Corning Glass Works list of sight glass molds. Continuous efforts have been made to keep down the number of sizes, but the success can be judged when it is shown that between the range of $2\frac{1}{2}$ in. diameter by $\frac{1}{4}$ in. thickness to $8\frac{1}{2} \times \frac{3}{4}$ in. it has been necessary to provide forty-one molds.

In the case of plant equipment, a further effort is being made to work out shapes which will suit a variety of uses, and it is hoped that

a full measure of cooperation will be extended by plant managers and engineers, through the use of stock rather than special molds.

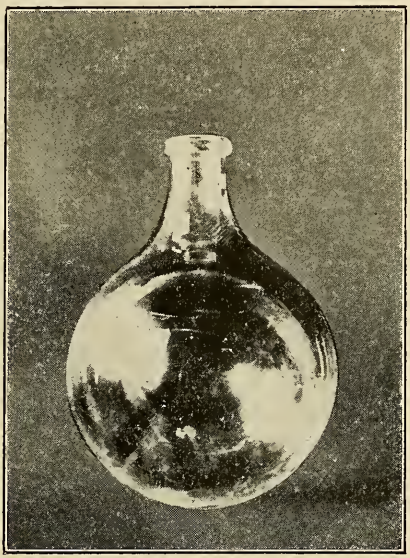


FIG. 4. A 72-Liter Retort

The industrial use of Pyrex is spreading into many fields, and while not a strictly chemical application, decided interest attaches to the development by the research laboratories of the Corning Glass Works of Pyrex high-tension insulators.

The generally accepted causes of failure of porcelain high-tension insulators are: (1) change in structure of porcelain with time and absorption of moisture; (2) breakage due to thermal changes; (3) flaws in the porcelain body, causing dielectric and other failures; (4) failure due to expansion of cements used in attaching hardware to the insulator; (5) mechanical weakness. These failures may be generally classified as failure due to the properties of the insulator and failure due to design.

Pyrex glass seems to have ideal properties for an insulator, for it apparently is not subject to any of the intrinsic weaknesses of the porcelain insulator. It does not change in structure, can be inspected for any defects, thus assuring a uniform product, has a sufficiently

high dielectric strength, a great resistance to thermal changes (its thermal expansion coefficient being lower than that of porcelain), and in addition is not heated by direct solar radiation as much as porcelain.

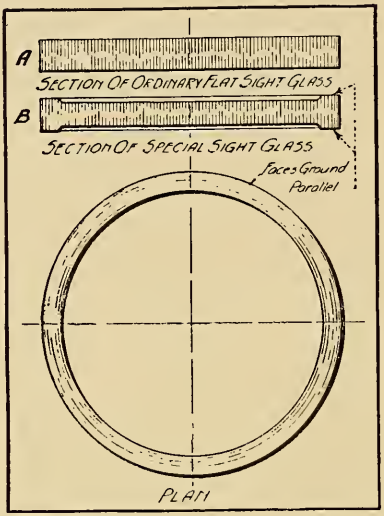


Fig. 5. Suggested Design of Pyrex Sight Glass

Consequently, if a Pyrex glass insulator could be built free from the design defects of the porcelain, there is no question that it would be a better insulator.

Fig. 6 shows the construction of the Pyrex insulator. It is evident at a glance that this construction and design gives a cement-free, all-metal and glass insulator, and that the design is one of great resistance to tension, as the material of the insulator is largely under compression.

Considerable data have been collected showing the relative properties of Pyrex.

Heating of glass and porcelain insulators by solar radiation shows a rise in temperature above air temperature for a porcelain insulator of 39.5 deg. C., and for a Pyrex insulator of 10.8 deg. C. This is a mean of ten observations in both cases. These data show the increase in temperature due to solar radiation to be 3.65 times as much for the porcelain as it is for the glass. The glass is transparent and the porcelain absorbs the heat radiation. This proves that in service the

glass is not subjected to anything like as severe heat changes as porcelain.

In a report on dielectric strength tests made by one of the large manufacturers of electrical equipment it was stated that unit No. 1 punctured at 143 kilovolts, unit No. 2 punctured at 160 kilovolts, and unit No. 3 punctured at 140 kilovolts.

"The tests on Pyrex suspension insulators show quite conclusively that the material has good characteristics. The uniformity of electrical puncture is a distinct advantage over porcelain."

It is evident that Pyrex glass has very good dielectric properties, more than ample for the service, as well as being uniform.

Tensile strength tests made by Cornell University, Sibley College, show:

No. 1.	22,600 lb.	No break
No. 2.	23,000 lb.	Pin broke in holding device
No. 3.	19,500 lb.	Pin broke in holding device, reaction broke insulator
No. 4.	22,750 lb.	Yielding, no break
No. 5.	23,600 lb.	Cracked
No. 6.	20,600 lb.	Click, no break
No. 7.	21,800 lb.	Click, cracked
No. 8.	22,000 lb.	No break
No. 9.	17,000 lb.	Click
	22,500 lb.	Click again, cracked
No. 10.	25,460 lb.	Broke stud, flange shattered by reaction, head O. K.

Since the better grades of porcelain insulators will not stand over 10,000-lb. load as a maximum, and many break below that, it is evident that the glass insulator has a strength far superior to anything yet developed. This property should allow for longer spans, and in many cases where two strings of porcelain are used in parallel one of Pyrex will be ample to carry the load.

Pyrex glass has a great resistance to water absorption and surface attack, and is therefore durable under long exposures to severe atmospheric conditions, as, for instance, around chemical plants.

It is probable that glass insulators will not be as attractive to birds and spiders for nesting sites, since they will not have the dark shadows that exist in a string of porcelain insulators.

The chief advantages of the Pyrer insulator are the fact that it does not absorb heat as does porcelain; has no cement in its construction gradually to absorb water and expand, ultimately fracturing the insulator; and has a mechanical strength that will average twice as high as any porcelain insulator yet on the market.

This paper describes in sufficient detail the present status of industrial Pyrex, and carries a suggestion of future possibilities. It is believed that Pyrex will in a short time occupy a definite place along

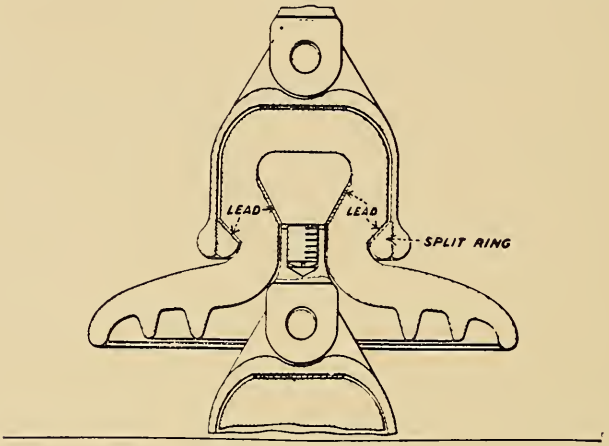


Fig. 6. Diagram of Pyrex Insulator

with the other materials used for plant construction. It is not a universal panacea for construction ills, but, like everything else in our practice, it demands thought in its application and care in its use.

Discussion

President Howard: This paper is open for discussion.

Mr. F. C. Zeisberg: I should simply like to confirm what Mr. Marshall said about the experimental denitrating tower which the du Pont company put in. We built this tower so that we could observe what was going on inside it. We expected to run it two or three days, and thought we would be lucky if we could run it that long. Everybody expected it would crack when we turned the steam on. We ran it several weeks at 170 degrees Centigrade. One day, while running, a hose burst and cold water was thrown so that it ran all over the tower. The tower has not cracked yet, and it has been a revelation to us to see the material stand up the way it has.

Mr. Huff: I want to ask if glasses such as Pyrex have been made which, when submitted to hot water for a long time, will not go to pieces? It has been my general experience in the laboratory that

glass apparatus immersed in boiling water will, after a few days, fracture very easily. Thermostat regulators, especially, give a great deal of trouble. I should be interested to know if Pyrex or any other glass does not have this disadvantage. I think that this property is exceedingly important in considering the uses of glass in certain types of plant installations, for example, water-scrubbing system running at high temperatures.

MR. MARSHALL: The bulletin I referred to in reading the paper is Bulletin 107 of the Bureau of Standards, which contains a rather complete summary of the action of distilled water, at the boiling point, on glasses. From the information given there, I take it that the action is much less on a boro-silicate glass than on glass belonging to the soda or lime group.

DR. WITHROW: I should like to ask Mr. Marshall a question. We have long known in the laboratory use of glass vessels, where there is a steam bath of live steam, that the vibration causes numerous nicks in a short time. I think this is important and I wondered how this glass stands the vibrations.

MR. MARSHALL: I don't know anything definite on this point because in the uses I have observed there has been no work under vibration. I take it, in your tower, Mr. Zeisberg, it was not under vibration due to the steam impact?

MR. ZEISBERG: For only a few moments. In starting up, until the water reaches the boiling point, there is a bumping, but after that there is no vibration.

DR. REESE: Are carboys made or in use of Pyrex glass?

MR. MARSHALL: That is one of the matters brought forward a few months ago, the matter of making up carboys, in view of the probable improvement they would represent. Through the use of a stress polariscope it is an easy matter to pick out carboys under strain. Experimental carboys will be available, I believe, about the week of Christmas, or possibly early in the New Year.

DR. REESE: I mention carboys because they are subject to vibration in transportation. They will be tried out in that way very quickly.

MR. MARSHALL: I think it would be easy to rig up some definite testing apparatus to carry out the result of Dr. Withrow's idea.

MR. HUGH K. MOORE: I should like to ask about the action of phosphoric acid at 250 degrees Centigrade. We all know there is a

great difference in glasses standing up at that temperature. We also know that even quartz would dissolve at that temperature, and while I don't expect Pyrex or any other glass will stand up at those temperatures, I wanted to know if Mr. Marshall has any data on it.

MR. MARSHALL: Yes; we went through the whole phosphoric cycle. We found Pyrex an improvement over other glass, but not worth talking about for construction purposes.

MR. JEROME ALEXANDER: I should like to inquire under what condition Pyrex glass devitrifies.

MR. MARSHALL: You get up to the initial softening point at 600 degrees Centigrade, and at that point you have no devitrification. In all the work we have done so far we have never been able to identify anything that, in quartz, we would classify as devitrification. The glass seems to be free from devitrification in anything that would be considered a working range.

MR. WADSWORTH: I should like to ask if the thicker walled Pyrex glass can be repaired with the oxyacetylene torch as the laboratory ware is repaired?

MR. MARSHALL: You can repair $\frac{3}{16}$ inch material satisfactorily, but I don't know what you can do with $\frac{3}{8}$ inch, as I have had no experience with this weight.

MR. HUBBELL: We frequently melt zinc in Pyrex beakers. The other day we bought an ordinary Pyrex baking dish and allowed it to float about in a galvanizing bath—taking it out now and then and placing it on the cold iron supports. The dish knocked around in the bath for two or three days and seemed none the worse at the end. I thought this might visualize the possibilities of Pyrex glass.

DR. PARSONS: I have nothing to add to the argument, but I think we, as Americans, ought to take great pride in the development of Pyrex. We really know very little of its merits yet. I know that abroad there is nothing of American development that is causing so much comment. The establishment of a plant for Pyrex in France shows what is thought of it there. I received many inquiries and comments about it in Europe this last summer. I doubt if anything in chemical engineering lines has taken place for many years of more importance than this great achievement which is solely an American development. [Applause.]

MR. MARSHALL: I want to thank you for the way in which you have received this paper. There is one thing I should like to add in

closing. Papers read before the Institute, as I see it, should always be papers free from anything in the way of advertising. It has been very difficult in preparing this paper to keep away entirely from something that might suggest that I was here to advertise the product of the Corning Glass Company. My intention has been to give to the Institute the line of development as far as it has gone, not solely because you may use the material, but because as engineers you should know something of this matter. I thank you. [Applause.]

PRESIDENT HOWARD: Mr. Marshall has advocated standardization of apparatus. This is a matter which is to-day being given careful attention by a committee of the Manufacturing Chemists' Association of the United States. They have already completed a report on the standardization of laboratory apparatus. That report has been printed and has been distributed quite widely. I think it is also to appear in at least one of the technical magazines. Now, our committee has not stopped work, and it would seem to me that it could very well take up the question of standardization of the very type of apparatus that Mr. Marshall has referred to. It would be very useful to have earthenware vessels so that they can be used interchangeably, and bends of Pyrex could be used to put into earthenware receivers. The personnel of that committee represents the largest chemical manufacturers in the country, and any work carried out by them would naturally have a great influence on the manufacture of that type of apparatus. The committee is under the chairmanship of Mr. Meiklejohn, of the General Chemical Company.

DR. REESE: The Standardization Committee of the Manufacturing Chemists' Association consists mainly of members of that Association, but they work very closely with the manufacturers of chemical apparatus, who have cooperated in a very splendid way and have even agreed to specifications for performance by which they will practically guarantee the accuracy of the apparatus that they supply. They are able to do this, knowing that they can make and keep the standard articles in stock, and that they will not be required to carry a larger number than under the specifications; so that I am satisfied that the specifications drawn up will be very helpful. The manufacturers have agreed, after testing a certain number, that the whole shipment will be accepted or rejected on the basis of this test.

PRESIDENT HOWARD: I will declare the discussion closed and we will now proceed to the business session.

INTEGRAL WATERPROOFINGS FOR CONCRETE

By ALFRED H. WHITE

Read at the Richmond Meeting, December 8, 1922

The conception of concrete which is perhaps still held by the majority of engineers and users is that of a mixture of Portland cement and inert aggregate which on reaction with water becomes a dense and hard mass, expanding and contracting in about the same ratio as steel with changes of temperature, but otherwise unalterable in volume and permanent if properly made and not exposed to any other action than that of water and air. It is now definitely established that concrete shrinks whenever it becomes dry and expands whenever it becomes wet, irrespective of the age of the concrete when tested, and that, furthermore, these changes in volume are much larger, more rapid, and more frequent than those due to temperature changes.[1] These changes in length when concrete is alternately wet and dried may amount to as much as the equivalent of a temperature change of 200° F.

Reactions of Portland Cement and Water

We may visualize the process of hardening Portland cement as follows: Each grain is surrounded by liquid water which attacks the surface of the grain, decomposes it, and forms hydrated compounds—silicates, aluminates, and hydrated lime, some of which are amorphous and some of which are crystalline. There is no sharp distinction between the setting and hardening process. These amorphous bodies are colloids. They swell when in contact with water and shrink when water is abstracted, just as clay does. As the author has shown in the above reference, concrete retains these properties of a colloid for at least 20 years to an undiminished extent. This reaction between the grains of cement and the water is so slow that it requires months or years for its completion. In a rich cement mortar the reaction stops only because the colloid has swollen to such an extent that no

[1] White, *Proc. Am. Soc. Test. Mat., 14,* 203–241 (1914). *Trans. Int. Eng. Congr.,* 1915, Vol. "Materials of Construction," pp. 242–273.

more water can force its way in to react with the unchanged kernels of cement. The pressure of this swollen colloid is enough to cause an increase in length of 0.15 per cent in bars of neat cement, and of expansion one-half as great in mortars of 1:3 composition. This expansion in 1:3 mortars is equivalent to a compressive stress of 1,500 pounds per square inch. Concrete which is properly made in a fairly rich mixture and thoroughly hardened under water will not permit any water to pass through it, because the swollen colloid closes all of the capillary pores. Such a concrete, when thoroughly swollen, will contain no liquid water, but only colloid water, or water of crystallization. If one surface of this concrete is in contact with water and the other in contact with air, as frequently happens in a dam or reservoir, the concrete will appear absolutely tight. No water will seep through it. If, however, instead of freely circulating air on one side of the concrete, the air should be relatively dead, as it might be in a cellar or basement, it would be found that the humidity of the air in the cellar was very high. Moisture would evaporate from the apparently dry surface of the concrete and be replaced by moisture diffusing through the colloid of the concrete. If the water were drained from the reservoir, in the case cited above, the concrete wall would lose water by evaporation from the colloid and shrink so that after a few weeks it would be porous. If the concrete wall were several feet in thickness, this phenomenon might not be noticed, but in a cellar wall twelve inches thick it might be very apparent. If, now, water should again be brought in contact with one side of the wall, the pores in the concrete would rapidly fill with water, due to capillary action, and the inside of the wall would appear damp. It might even allow water to percolate through it for a few days until the dehydrated colloid had again absorbed water and become swollen so as to shut out further ingress of water. It has been the tendency of engineers to test concrete when it is wet, and most of the results which have shown concrete to be waterproof have been made on concrete with its colloid fully swollen.

Scope of This Paper

The present paper will deal with the properties of concrete and of integral waterproofings, not as used under conditions where the concrete is always kept wet, but as used where the concrete is frequently dry and indeed may never have had adequate opportunity to have its

colloid developed. The present paper limits itself quite closely to a discussion of the rate of absorption of water by capillary action and the effect of integral waterproofings on the rate of water absorption. The results set forth were obtained by observations on blocks 4 x 4 x 6 in. made from a single lot of sand and with cement from well-recognized commercial brands. The sand was clean, natural sand of good quality. The blocks were all made from a 1 : 3 mix with about 10 per cent of water. The tests which are presented here are selected from a total of 98 involving differing materials and different methods of treatment. In many cases discs were made for permeability tests, but the results were so discrepant that no mention is made of them here. Selection of tests on the blocks has been made with a view to showing changes which are believed to be typical of the whole series.

Water Absorption by Mortars with No Waterproofing Agent

The behavior of a block of 1 : 3 mortar without waterproofings is shown in Fig. 1. This block, 160 B, was made from one volume of Universal cement, three volumes of sand, and one volume of water. It was mixed by hand and placed in a metallic mould 4 inches square and 6 inches deep. After 12 days in the mould it was removed and allowed to dry 21 days in the air, during which period it lost 3.87 per cent in weight. It was then placed in a box containing a layer of damp sand with a constant water level ¼ inch below the surface of the sand. The block was placed on end on the surface of the sand and the box was covered with a cloth so that evaporation was largely restricted. During 13 days on damp sand the block gained 8.1 per cent in weight. The detail shown in the lower part of Fig. 1 indicates the rise of moisture in the block. After 9 hours, moisture had risen 4 inches out of the total 6, and at the end of 24 hours the top of the block was moist. At this time the weight was 0.54 per cent less than the initial weight of the block when it was removed from the form. The capillaries were not, however, completely filled with water, for the block continued to gain weight at a decreasing rate until after 13 days its weight had increased to + 3.75 per cent. It was then immersed in water and in 10 days increased only 0.5 per cent more. It is thus apparent that a cement mortar even as rich as 1 : 3, which is allowed to dry out when removed from the forms, is highly absorptive.

This block was then allowed to stand in the air of the laboratory

for 9 months, when it was again placed on damp sand. Its dry weight was practically the same as in the previous year, but it only absorbed a little over one-half as much water, and the moisture only climbed 4½ inches in 10 days, whereas in the preceding year it had climbed

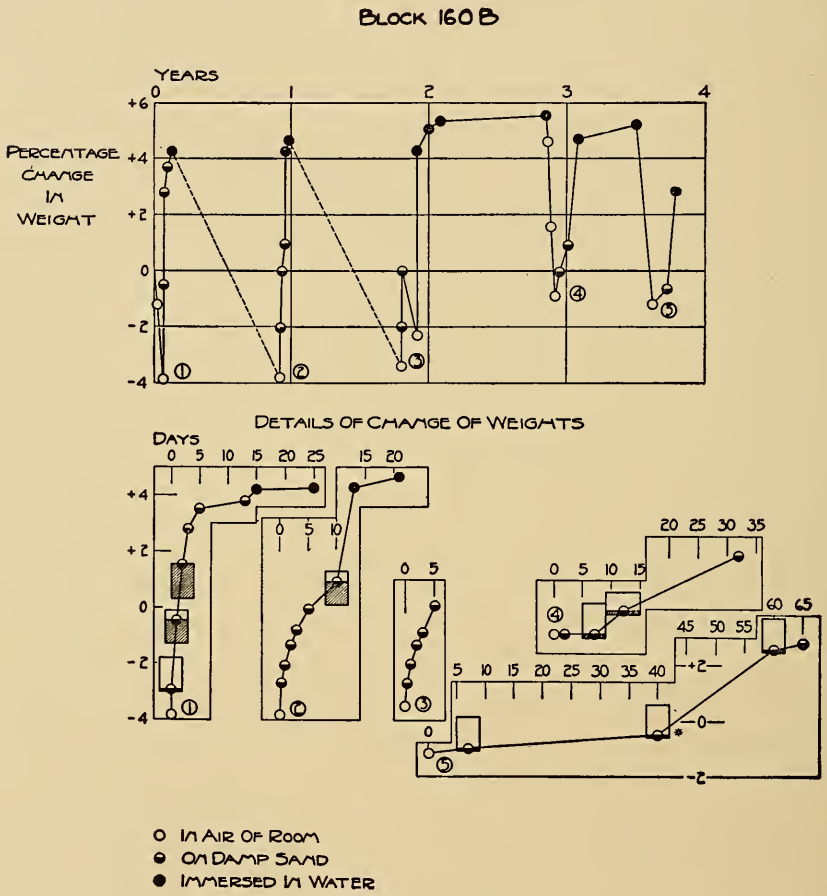


Fig. 1. Behavior of a Block of 1:3 Mortar Showing Changes in Rate of Water Absorption with Age. The Bottom of the Block Was Rasped Off.

6 inches in one day. On immersion in water for 10 days the weight increased to an even slightly higher figure than it had reached in the preceding year.

This block was then again dried for 10 months in the air, when

it returned to nearly the same dry weight which it had shown originally. When placed on damp sand it absorbed moisture at substantially the same rate as before. It was then determined to try the effect of a longer immersion in water and it was kept continuously under water for 11 months. During this immersion its weight increased slowly through hydration of cement which had not been preiously attacked. When dried 25 days in the air, after its 11 months' immersion in water, it retained almost as much moisture as it had held when it was first removed from the mould. This is a clear indication that the colloid had developed by the 11 months' immersion in water. When this block was now placed on damp sand, the moisture climbed only ¾ inch in 6 days. The block was then laid on its side instead of its base, but the water climbed only ½ inch. The block was again immersed in water for 5 months and then kept in air for 45 days, when it was again placed on damp sand. The moisture only rose ½ inch in 40 days and the change in weight was almost negligible. It was evident that for some reason the moisture was no longer rising in the block. The query then arose as to whether the resistance to the absorption of water was in the skin of the block or was uniform throughout the entire mass. To determine this point, about ⅛ inch was rasped off the bottom of the block and it was again placed on damp sand. Its behavior is shown in Detail No. 5 of Fig. 1. The block now absorbed moisture rather slowly until its total increase in weight was greater than it had been on its first test when the water had reached the top of the block. Notwithstanding this fact, the surface of the block remained entirely dry except for the damp line about ¼ inch wide at the bottom of the block. The conclusion is that the non-absorptive properties resided largely in the skin of the block. The earlier test had shown that the side of the block was not more permeable than the base of the block, so that it could not have been due to any accidental contamination with oil or other water repellant material on the base of the block. The explanation may be easily found from consideration of the theory. One of the products formed by reaction of Portland cement and water is hydrated lime. This is relatively soluble in water. When the block with its pores filled with water is allowed to dry in the air, it is not pure water that travels to the surface of the block, but a saturated solution of calcium hydroxide. This becomes converted to calcium carbonate through reaction with the carbon dioxide of the air, and the calcium carbonate thus

deposited seals the capillary openings just as on a larger scale it stops up the tubes in a steam boiler. The surface of good and fairly rich concrete which is alternately wet and dried will therefore waterproof itself in time through deposition of calcium carbonate. The waterproofing will, however, reside mainly in the skin, and the center of

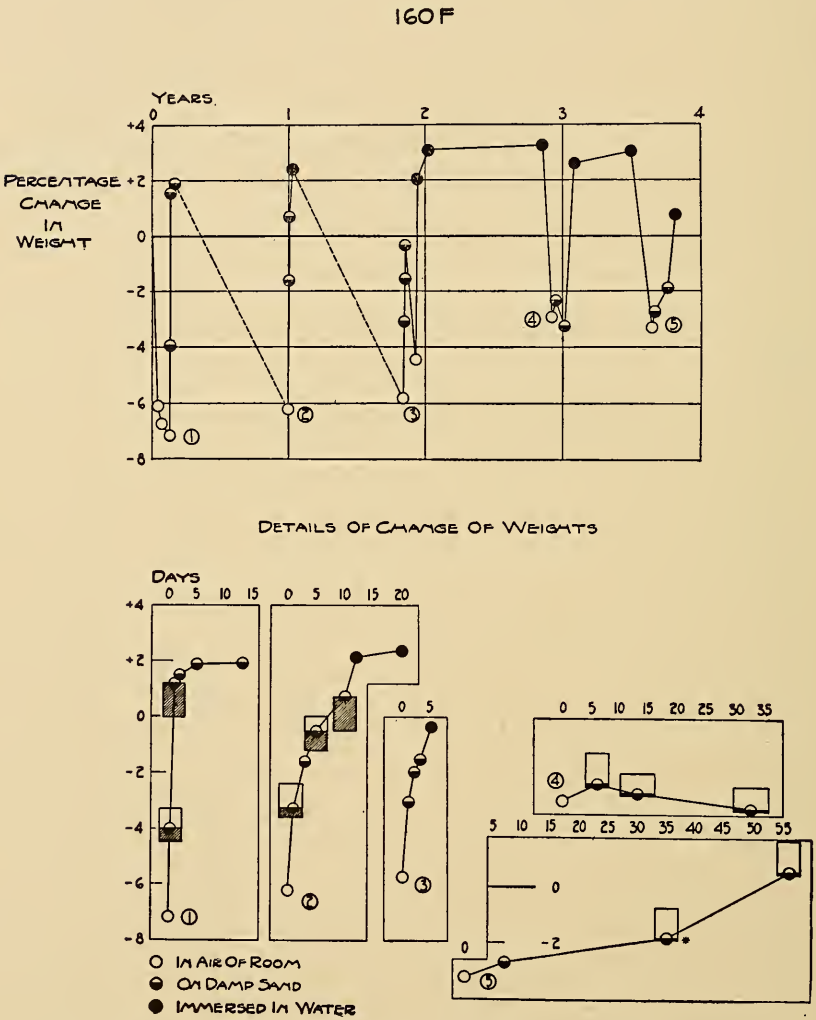


FIG. 2. Effect of Addition of 10 per cent. Hydrated Lime on the Rate of Water Absorption by a Block of 1 : 3 Mortar at Various Ages. The Bottom of the Block Was Rasped Off.

the mass will still have capillary openings. These capillary openings will, however, be smaller in old concrete which has had long immersion in water, because they have become partly filled with colloid. Dry concrete will, however, always have capillary canals.

Effect of Hydrated Lime

The effect of hydrated lime is shown in Fig. 2, which is a study of a block made from 1 volume of cement and 3 volumes of sand, to which was added 0.1 volume of high calcium hydrated lime for each volume of cement. This block, 160 F, was kept two days in a metal mould, then dried in the air of the laboratory for 38 days, and then placed on damp sand as before. The absorption of water was, roughly, three times as rapid as in the case of the mortar to which no lime had been added. After 10 months in air, the test was repeated and the absorption found to be distinctly slower than at first. After the block had stood 11 months in water and had been afterwards dried for 28 days in air, a repetition of the absorption test showed very little increase in weight. This is shown in Detail 4 of Fig. 2. When the block was placed on its side instead of its base, it actually lost weight because of the better conditions for evaporation. After another period of 5 months in water and subsequent drying, the block was again placed on damp sand. There was very slow absorption. When, however, after 35 days on damp sand with very slow absorption the outer skin of the base was rasped off, the weight increased much more rapidly, as shown in Detail 5 of Fig. 2. The final waterproofing was due largely to deposition of calcium carbonate in the pores of the surface, as in the previous case. The first effects of hydrated lime are distinctly unfavorable when considered from a waterproofing standpoint. Hydrated lime is a water-absorbent colloid and the addition of this material promotes absorption of water until such time as the surface pores become filled with calcium carbonate.

Effect of Clay

The effect of clay is shown in Fig. 3, where the history of Block 159 Z is traced. This was made from 1 volume of cement and 3 volumes of sand, with the addition of a plastic clay to the extent of 15 per cent of the weight of the cement. The clay caused an absorption even more rapid than hydrated lime on the early tests. The

rapid absorption persisted even on the later tests, as shown in the details of Fig. 3. This block only received an immersion of 2 months

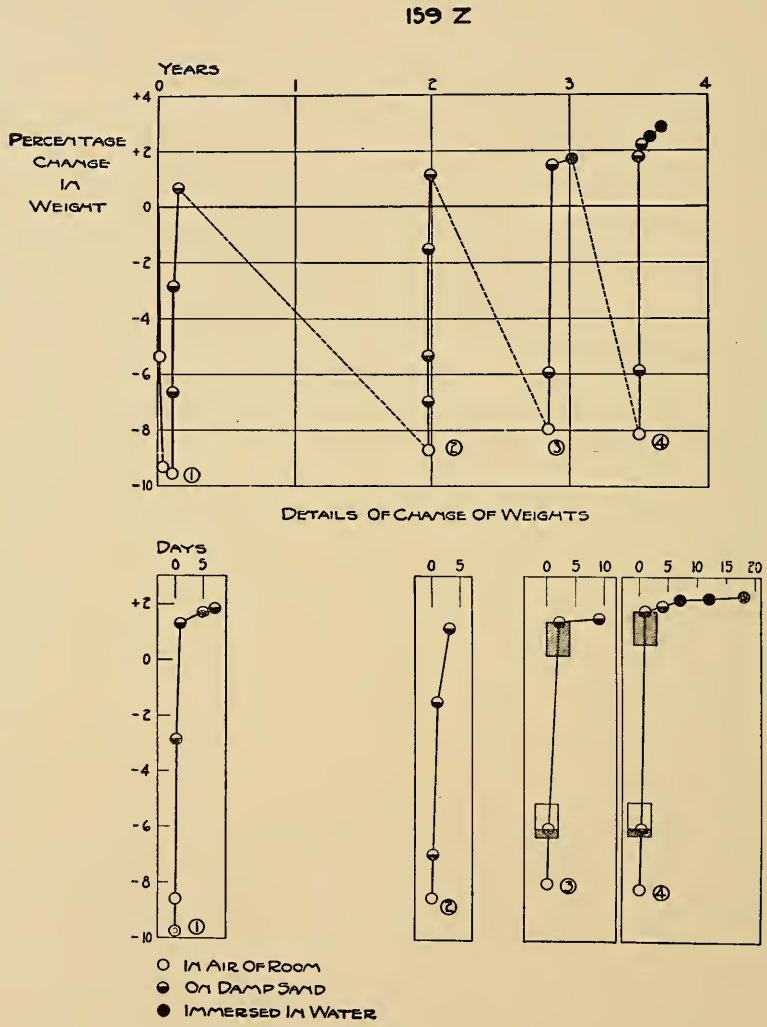


FIG. 3. Effect of Addition of 15 per cent. Clay on the Rate of Water Absorption by a Block of 1:3 Mortar at Various Ages.

instead of the 11 months' immersion given to the blocks of Figs. 1 and 2 in the third year, so it is not possible to say whether it would ultimately have become non-absorbent. Clay certainly makes a much

poorer showing than hydrated lime, which, in turn, does not make so good a showing in its earlier career as the mortar containing only cement and sand.

Effect of Petroleum Residuums

The influence of petroleum residuums of various sorts was tested and Fig. 4 is represented as a typical case. Block 160 T was made

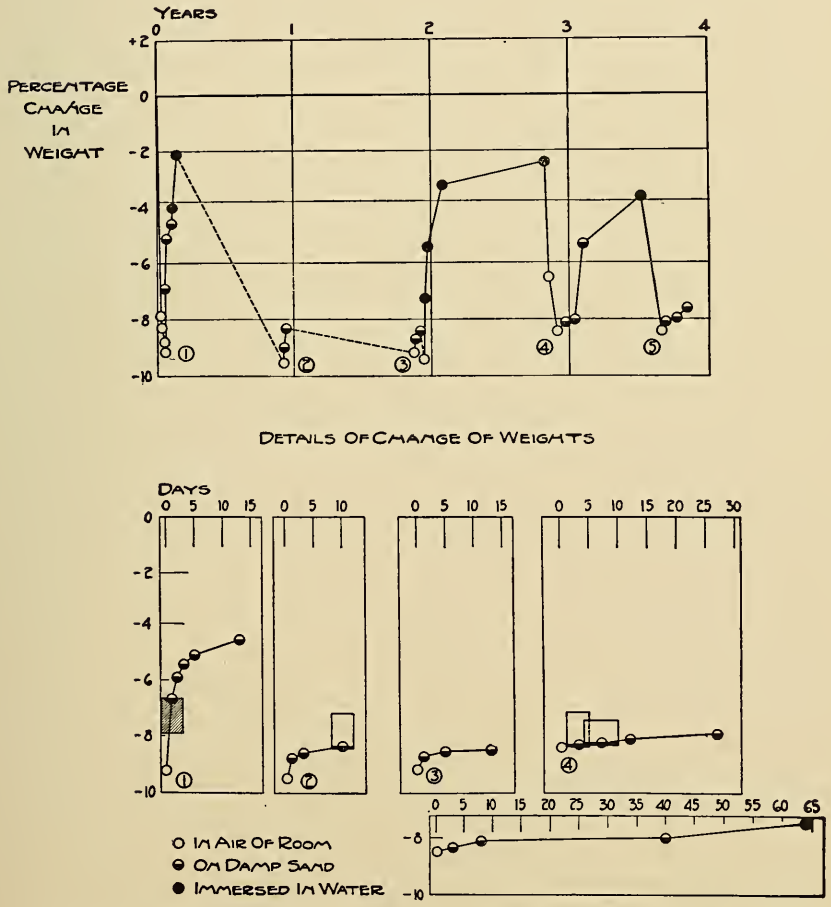


Fig. 4. Effect of Addition of 10 per cent. Heavy Petroleum on the Rate of Water Absorption by a Block of 1:3 Mortar at Various Ages.

from 1 volume of cement and 3 volumes of sand, with the addition of a mixture of mid-continent semi-asphaltic flux thinned with 10 per cent of its weight of benzene to make it more miscible. This diluted flux was used in the proportion of 11 per cent of the weight of the cement. The block was dark in color and smelled of petroleum. The water absorption on the early tests was distinctly slower than in the cases previously discussed, although the moisture rose to the top of the block on the first test. The second and subsequent tests showed very efficient dampproofing. Even after the bottom of the block was rasped off on the fifth absorption test the increase in weight was very small. An objectionable feature was noted in the diffusion of the oil out of the block. After the block had stood for several days on damp sand, the sand would be black from diffused oil for a depth of one-quarter of an inch below the block.

Effect of Insoluble Soaps

The insoluble soaps tested as waterproofing agents were prepared in the laboratory by precipitation, washing, and drying. This had the advantage of the use of a definite product, but the disadvantage of the difficulty in mixing it with the water. The soaps were distinctly water repellant and did not lend themselves as well to incorporation as some of the commercial compounds especially prepared to emulsify readily with the mixing water.

The behavior of calcium oleate as a dampproofing agent is shown in Fig. 5, which shows the behavior of Block 159 B made from 1 volume of cement, 3 volumes of sand, and calcium oleate to the extent of 1 per cent of the weight of the cement. This dry calcium oleate was flocculent and did not emulsify at all readily. The first water-absorption test showed distinctly less absorption than the blocks which did not contain any water-repellant material. Later tests showed the same property. This block did not receive any immersion to develop its colloid until the end of the third year, and then it was kept only 30 days in water. After drying it was again tested for water absorption and increased in weight slowly until after seven days the water reached the top of the block. It was then put into water for a longer time, but unfortunately the test had to be interrupted at that point.

The effect of aluminium stearate is shown in Fig. 6. Block 159 F was made, as the others, from a 1 : 3 mix, with the addition of aluminium stearate to the extent of 1 per cent of the weight of the cement.

An attempt was made to emulsify the aluminum stearate with dilute ammonia, but with only partial success. The tests parallel those with calcium oleate shown in Fig. 5, but are in general more favorable.

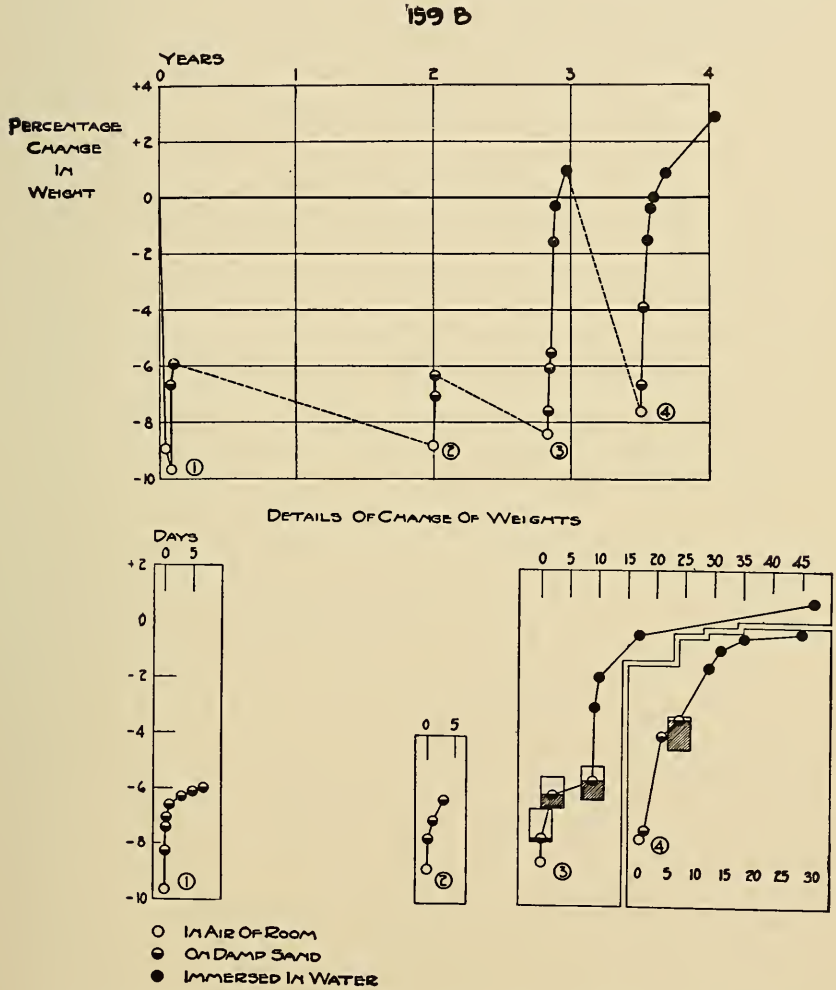


FIG. 5. Effect of Addition of 1 per cent. Lime Soap on the Rate of Water Absorption by a Block of 1:3 Mortar at Various Ages.

The difference is not large enough to be decisive and may well be due to the better emulsification of the aluminium soap.

Comparison of Water Absorption

A comparison of the behavior of these blocks during their first absorption period is given in Fig. 7, where the rate of water absorption of the air-dried blocks when placed on wet sand is plotted. It will be noted that the three blocks, with the insoluble soaps and with

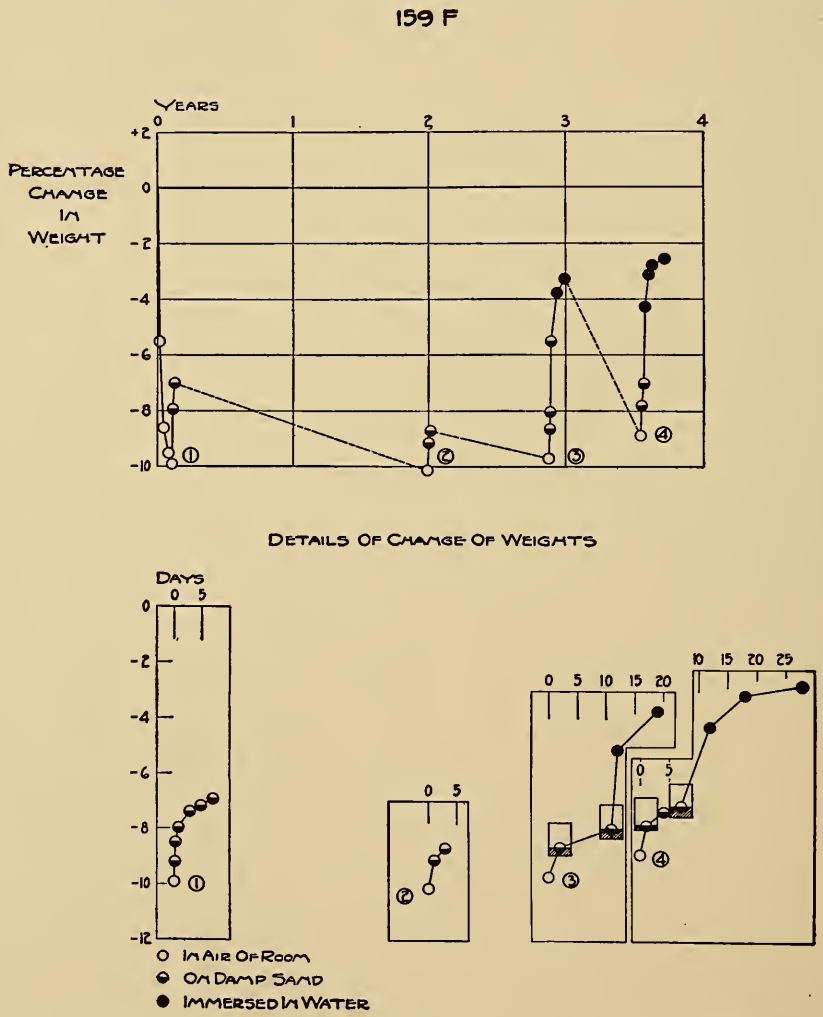


Fig. 6. Effect of Addition of 1 per cent. Aluminium Soap on the Rate of Water Absorption by a Block of 1:3 Mortar at Various Ages.

petroleum incorporated, show roughly only half the absorption of the plain mortar, which in its turn makes a distinctly better showing than the blocks containing hydrated lime or clay.

Influence of Intergal Waterproofings on Strength

The question of strength of mortar and concrete treated with integral waterproofing is of prime importance. Abrams[2] reports that hydrated lime and clay both weaken concrete to a rather small

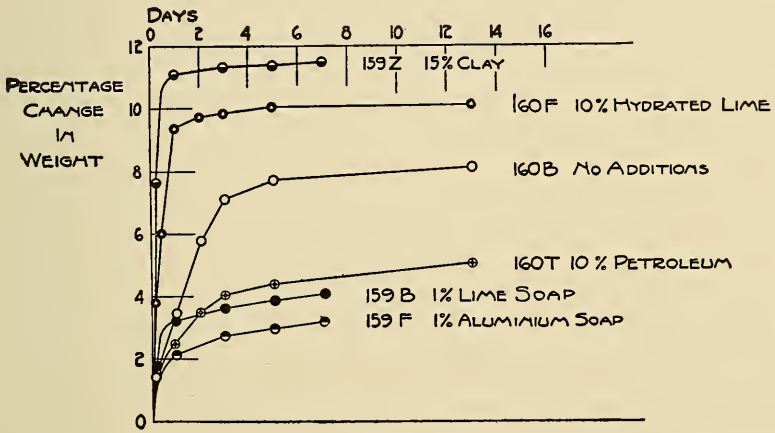


Fig. 7. Comparison of Rate of Water Absorption of Various Blocks of 1:3 Mortar Containing Additions as Shown, and Placed When Dry on Damp Sand.

extent. The experiments which are given in the present paper do not warrant the consideration of hydrated lime and clay as dampproofing agents. The effect of water-repellant integral waterproofings on strength has not had the same recent and careful study which Abrams has accorded the others. The action of insoluble soaps was carefully studied in Technologic Paper No. 3 of the Bureau of Standards issued in 1911. Both tensile and compressive strengths of mortar of varying richness containing commercial waterproofings whose chief constituent was an insoluble soap mixed with dry hydrated lime were included in this report. The investigators at the Bureau of Standards drew the conclusion that the strength was not seriously affected by the compounds used. There were seven of these waterproofings containing insoluble soaps and the amount of fat acid

[2] *Proc. Am. Soc. Test. Mat.*, 20, II, pp. 149–203 (1920)

varied from 0.064–0.78 per cent of the weight of cement used. It is very difficult to get a clear picture of the effect of these compounds from the long tables given in this Technologic Paper No. 3, and in order to give a visual picture of this effect the results have been

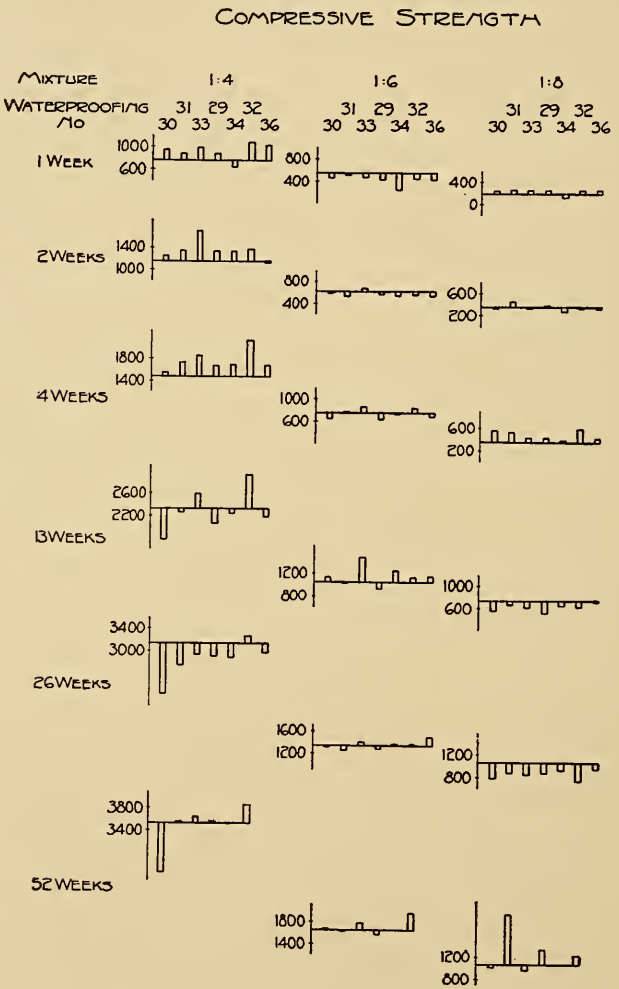


FIG. 8. Comparison of Compressive Strength of Concrete Containing Various Amounts of Lime Soaps. The Horizontal Line Shows the Strength of the Concrete to which No Additions Have Been Made. The Rectangles Show the Differential Strength of the Specimens Containing Waterproofings. Data from Technologic Paper No. 3 of the Bureau of Standards.

plotted in Fig. 8. In this figure the compressive strength of the non-waterproofed specimen has been shown by horizontal lines. The variation of the samples containing waterproofings is shown by rectangles extending above or below these horizontal lines. The waterproofing agents are arranged in increasing order according to their fat acid content. The figure may be further explained as follows: The first column of Fig. 8 shows the compressive strength of blocks of 1:4 mix, kept damp for varying periods. The average compressive strength of the non-waterproofed specimens tested when one week old was 750 pounds per square inch. Six out of the seven waterproofed specimens showed a higher compressive strength than the mortar with no additions. The highest figure, for No. 32, was 1,096 pounds. A similar picture was presented at the end of two weeks and of four weeks. In testing at the end of 13 weeks, two waterproofed samples showed better than the non-waterproofed and four did not show so well. After 26 weeks only one of the waterproofed samples showed a better strength than the non-waterproofed. At the end of 52 weeks only five samples were tested. Four of the five showed higher strength than the non-waterproofed mortars.

The compressive strength of the 1:6 and 1:8 mixes, as shown in the second and third columns of Fig. 8, reveals much the same picture. It must be remembered that the base line is the compressive strength of the non-waterproofed mixtures, and that any error in this base line would distort the whole series in which that particular test was used as base. Judgment must, therefore, be formed on the picture as a whole. The tests on the leaner mixes 1:6 and 1:8 show, with a few exceptions, rather slight variations from each other and from the non-waterproofed samples. Tests on the 1:4 mix show uniformly greater strengths at one, two, and four weeks. The results at 13 weeks scatter, those at 26 weeks are inferior to the non-waterproofed samples, while four out of the five waterproofed samples tested after 52 weeks were stronger than those not waterproofed. This considers all the different waterproofings as being of equal merit. This is, however, hardly fair. The mixtures containing waterproofing No. 30 only contained 0.066 pound of fat acid for each 100 pounds of cement. This mixture No. 30 gives inferior results. On the other hand, the mixtures containing waterproofing No. 32, which contained 0.75 pound of fat acid for each 100 pounds of cement, showed distinctly

higher compressive strengths than the non-waterproofed samples of the 1:4 mix at each one of the six test periods.

The author has not made nearly as complete a series of tests of strength as those reported by the Bureau of Standards, but he has been puzzled to find similar instances of higher strengths on the part of mortars containing small amounts of insoluble soaps. It is not easy to see why insoluble soaps should increase the strength of mixtures kept constantly wet or damp as was the case in the tests of the Bureau of Standards. It is, however, possible to see how any type of water-repellant integral waterproofing may increase the strength of concrete or mortar left in air after removal from the mould. A water-repellant material diminishes the flow of water to a dry surface by capillary action in the same way that it diminishes absorption from a wet surface. Therefore a block of mortar containing a water-repellant material will not dry out as rapidly as one which does not contain such a material. It should, therefore, have a better opportunity to develop its colloid and should show higher strengths, especially at the end of 7 and 28 days in air.

Summary

When Portland cement reacts with water it forms a colloidal body which shrinks when it dries and expands when it becomes wet. This property persists for at least 20 years and probably keeps on indefinitely. These changes in volume, due to moisture only, are frequently equal to those produced by a change in temperature of 200° F. The only way to prevent them is to keep the moisture of the concrete constant in amount. Where the concrete is under water this is easily accomplished. Portland cement in contact with water hydrates very slowly and it is only after months that the reaction ceases. In good, dense concrete the reaction stops because the capillary pores are packed so full of the colloid developed from the cement that no more water can enter. Therefore, ordinary good concrete kept constantly wet becomes impervious to water after several months without any waterproofing agent. However, if one side of a reservoir, for instance, is exposed to the air, there will be continuous evaporation from the apparently dry wall and the water evaporated will be replaced by diffusion through the colloid. If a concrete cellar should be constructed in wet soil, the wall should ultimately become tight so that no liquid water should seep through. The air of the cellar would, however, always show a high humidity.

Concrete which is dry is porous and therefore permeable to water. If this concrete has previously been immersed in water for several months so that the colloid has been well developed previously, the colloid will swell rapidly and soon become impermeable. It will remain so as long as it stays wet. If the concrete has only had short prior immersions in water, the concrete will retain its porosity until the colloid swelling by longer exposure to water closes the pores. Concrete which has once had its colloid fairly well developed so that the capillary pores are small may form a waterproof skin if it is alternately wet and dried. When concrete is wet the water absorbed dissolves hydrated lime, which is one of the decomposition products of the cement. When the concrete dries this dissolved hydrated lime is brought to the surface and changed to calcium carbonate through contact with the carbon dioxide of the air. This calcium carbonate deposited at the surface of the concrete fills the surface pores and in time waterproofs the concrete quite effectually so long as the surface skin is intact.

It takes a number of systematic alternations between the wet and dry state to form this waterproof skin, and ordinary mortar, even as rich as 1:3, absorbs water rapidly during its early life. Lean or carelessly mixed mortars may never become waterproof in this manner.

Various compounds have been proposed for incorporation in the concrete mixer as integral waterproofings. They are of two types. The water-absorbent class is represented by hydrated lime and clay. The water-repellant class is represented by mineral oils and insoluble soaps. Hydrated lime and clay ought really to be classed as negative waterproofing materials, for they absorb water more rapidly than the mortar to which they are added. In course of time mortar to which hydrated lime has been added will waterproof itself through development of the colloid from the cement and deposition of calcium carbonate in the surface pores precisely as if no hydrated lime had been added. Perhaps mortar with added clay will also become waterproof in the same way, but the action is certainly delayed.

Water-repellant waterproofings of the type represented by heavy petroleum oils and insoluble soaps diminish the capillarity of the pores in the dried mortar or concrete, so that perhaps only half as much water will be sucked up by capillary action. These waterproofings, when used in the small percentages advocated for commercial use,

may not prevent the capillary pores from being filled with water if pressure is applied or even if the concrete is immersed in water. Their efficacy depends more on the manner of preparation than on chemical composition. The proposal has been made to call these "dampproofing" rather than "waterproofing" materials and there is considerable ground for using this term. The designation "integral waterproofings" is, however, well established. Petroleum oils possess the disagreeable property of diffusion to the surface of the block. The insoluble soaps do not possess this inconvenient property. They are resistant to decay and may fairly be considered as permanent additions to the concrete. If the concrete is kept wet, the development of the colloid of the cement will take place just as if no compounds had been added. If the concrete containing insoluble soaps becomes dry and later is brought in contact with damp sand, the absorption of water by capillarity is greatly reduced.

The use of small quantities of these insoluble soaps does not decrease the strength of concrete. Theory would indicate that concrete containing water-repellant materials should dry out more slowly when exposed to air. Therefore, concrete exposed to air as soon as the forms were stripped should have a better opportunity to develop its colloid during the first few weeks if a small amount of water-repellant compound had been incorporated, since the rate of evaporation of the water would be slower. There is perhaps hardly adequate confirmation of this theory, although some tests made by the author confirm it. The elaborate tests reported in Technologic Paper No. 3 of the Bureau of Standards fail to indicate any harmful effects of insoluble soaps on the strength, and in some cases show distinct improvement in strength of mixtures to which insoluble soaps in small amount have been added.

The conclusion is that integral waterproofings of the water-repellant type have a distinct field of usefulness in conditions such as are found in foundations where concrete is sometimes dry, and sometimes, when dry, is suddenly wetted on one side.

Department of Chemical Engineering,
University of Michigan,
Ann Arbor.

Discussion

Dr. Jerome Alexander: There are two very interesting points that have come out in this paper. One is a typical illustration of the capillary phenomenon pointed out by Professor Bechhold a few years

ago in a paper published by him in the *Kolloid Zeitschrift*. Bechhold took some plaster of Paris blocks and immersed them in sulphate of copper solution. Upon breaking some of them in two you could see that they were colored all through. Then he allowed the blocks to dry, and after they had dried he broke them open and was surprised to find that there was no copper left on the inside of the blocks. He could not get even a qualitative test for copper on the inside. As the moisture had evaporated it had taken with it all of the copper, and that is apparently what has happened with the calcium hydroxide in these experiments.

Another principle is involved in this work. Just as wet sand is more coherent than dry sand, so, too, if free moisture remains within the concrete, the concrete will be stronger. But the moisture remaining inside is undergoing a slow combination with the chemical constituents of the concrete, and this accounts for the fact that the results vary with time. I offer these suggestions so that Professor White may consider his data in view of them.

Mr. Wadsworth: I should like to ask Professor White if he has had extensive experience with the compressive strength test? Recent contact with the Portland Cement Association reveals the fact that they are rather strongly opposed to the compressive strength test. I don't think they want to introduce into their standards the compressive strength test, and I wondered whether Professor White's experience with it had been extensive enough to vouch for its reliability as a test for Portland cement?

Professor White: It is my understanding that the Portland Cement Association in their research laboratory in Chicago use the compressive test very largely, and that their objection is to introducing it as a standard test for testing Portland cement. The objection to the compressive test in the standard specifications is mainly because of the difficulty of using that test in the field. It is a rather more difficult test to make. The Portland Cement Association has, to my mind, a very great field in trying to improve its products. There are differences in Portland cement. The various lots and brands may be all passable, but some are better than others. It is not always a fair deal, when a Portland cement structure shows disintegration, to say that a contractor did a poor job, because it is not always the contractor's fault.

Dr. Bartow: I noticed a short time ago that in lining the reservoir

of the water company at Omaha they used soap and alum in waterproofing. I should like to know whether Professor White thinks that is worth while, and also whether in the lining of a wood reservoir it would really be profitable to do it, because apparently it is only capillary action that carries the water through.

PROFESSOR WHITE: Wasn't it a coating of alum?

DR. BARTOW: No; it was mixed up.

PROFESSOR WHITE: You can buy on the market an emulsion of an aluminum soap which is better than a compound resulting from two materials mixed on the job. The commercial articles on the market have been prepared with care to get as high a degree of dispersion as possible. A reservoir filled with water all the time ought not to need waterproofing, except above the water line, where waterproofing might be required.

PRESIDENT HOWARD: Does the tensile strength of old concrete vary as it dries out and wets again?

PROFESSOR WHITE: Yes; that has been shown by several people. Careful tests were made by Van Ornum in St. Louis about eight years ago. He made a number of standard cylinders and tested them all when they were forty days old. He kept some of them in water for forty days, and he kept some of them in air for forty days, and some of them he kept in air for part of the time and in water for part of the time. He took the results of compressive strength of those kept constantly in air at 100. On that basis the compressive strength of those kept in water was something like 150. But those that had been in air for varying times and in water for varying times, instead of showing results lying in a straight line between 100 and 150, showed a sharp drop in strength with a minimum of about 65 for cylinders which had been in air 37 days and then in water 3 days immediately before being tested. Those cylinders immersed in water three days had had the colloid of the outer ring expanded, so that there was a shearing stress in that cylinder before it went into the testing machine. The outer shell was expanded and the core contracted so that the strength was only two-thirds of those dry all the time, and about one-third of those in water all the time. In at least one case, where a building collapsed during construction, it was claimed that a heavy rain coming on the concrete at a critical time caused the concrete to weaken enough through this expansion to collapse, where under normal circumstances it would not have collapsed.

THE USES OF CONCRETE IN CHEMICAL WORKS

By A. C. IRWIN,

Read at the Richmond Meeting, December 7, 1922

The chemical engineer is not limited in the scope of his interest to that which pertains only to processes of manufacture of chemical products. On him rests, or should rest, the main responsibility of constructing facilities best suited to the various processes of chemical manufacture, and in this respect concrete holds especial interest to the chemical engineer. In fact, the active portion of concrete, namely, Portland cement, is produced of standard quality through the guidance and advice of the chemical engineer.

The properties of building material and the methods of design of structures are matters of more or less perfect knowledge, but when we consider the use of certain materials which must be the containers of an almost endless variety of chemicals and chemical compounds, or which must receive and resist both chemical action and abrasion from traffic of one sort or another, we find available little positive research knowledge. The effect of chemicals on the construction materials proposed for use, and how we may know beforehand what materials or combination of them will best serve the particular purpose intended, are matters of vital importance to the engineer who is responsible for construction in chemical works.

Concrete is a comparatively new construction material, but nevertheless has been used for more separate, distinct purposes than any other. It is simple yet complex. Simple in that the ordinary processes of its making followed in the past have been carried on successfully by unskilled workmen, and in that the more scientific and perfect methods now known to give remarkably greater strength and resistance of all kinds may still be followed by ordinary workmen under competent supervision. It is complex in that at least one of its ingredients, and that the fundamentally important and active one, namely, Portland cement, is the result of chemical processes which to this day are not completely understood.

The compounds resulting from calcination to incipient fusion of

an intimate mixture of finely ground and properly proportioned argillaceous and calcareous materials are fairly well known. These compounds are, principally, tri-calcium silicate, di-calcium silicate, and tri-calcium aluminate. The exact steps in the chemical combinations of the materials to form these compounds are not known fully or with exactitude. When these silicates and aluminates with a small amount of gypsum are ground together to the fineness of impalpable dust, or to be more exact, so that 78 per cent will pass a 200-mesh sieve, we have Portland cement.

We know that Portland cement, when subjected to a sufficient amount of moisture at a proper temperature for a sufficient period of time, enters into chemical combination with water and forms a solid, hard, strong, crystalline mass having great binding power. Upon the stability of these new chemical compounds depends largely the adaptability of concrete for use in chemical works, and especially in those places where it comes in contact with chemicals of an active nature.

It is well known that certain acids and other chemicals act upon most natural stones and upon concrete. Any chemical action on concrete must result from the affinity of the acid or other chemical to the compounds resulting from the reaction of cement and water, or to the aggregate in the concrete, or to both.

It is obvious that each particular case requires special consideration in order to determine whether special treatment of the concrete with a protective substance is necessary, or whether the stored chemicals are neutral with respect to the concrete and therefore require no surface treatment or protection of any sort. Due to the continual progress in the art of making concrete no definite line can be drawn from past experience between those conditions which demand protective treatment, regardless of the quality of the concrete, and those which need nothing more than the manipulation of the materials to obtain the best possible quality of concrete. In general, whatever extra trouble is required to proportion the materials correctly, mix them sufficiently, and cure the concrete properly, is many times compensated for in the increased strength, greater wear resistance, and immunity from attack by penetrating chemicals, and in greater permanence under all conditions.

It is not possible to include within the limitations of this paper a detailed description of all the reasons for the things to be observed

in the manufacture of the highest quality of concrete with given materials,[1] but in the construction of tanks only the very best results obtainable should be accepted. If the methods necessary for best results were complicated, some reason would exist for not attempting them, but there is absolutely nothing complicated about determining the fineness modulus, the proportions, including water, or measuring plasticity by the slump test. The aggregate should be chosen with reference to its neutrality in its natural state to the liquid or chemical with which the concrete will come in contact. The mixing should be continued until perfect homogeneity is obtained. The amount of mixing water should be a minimum to produce a workable plastic mix. The concrete should be tamped solidly in the forms, and should be protected against loss of mixing water by keeping it constantly damp. In other words, use less water in the mix and more in the curing. One pail of water more than necessary will reduce the strength of the resulting concrete as much as leaving out two pails of cement. The aggregate should be not only clean, as indicated by the decantation test, but what is more important, should be free from organic impurities as determined by the Abrams-Harder colorimetric test for organic impurities in sands.[2] Tests show that one-tenth of one per cent of tannic acid in sand may reduce the compressive strength of the concrete by 25 per cent.

Watertightness is of prime importance for all liquid containers, and watertight concrete can be obtained with certainty. Concrete that is very porous obviously will not prevent the passage of water through it. If we know the causes of porosity, we can obviate it by removing the causes.

Porosity may be due to insufficient cement to fill the voids in the sand or insufficient mortar to fill the voids in the coarse aggregate, or both. Even though sufficient cement and sand are used, porosity may still exist due to insufficient mixing, improper placing, or the use of too much water in the mix. Insufficient mixing leaves unfilled voids in the stone or sand, or both, because of the presence of too much cement or mortar in one part of the batch and not enough in

[1] For complete discussion see bulletins of the Structural Materials Research Laboratory, Lewis Institute, Chicago, Ill., and various publications of the Portland Cement Association, Chicago, all of which may be had on request.

[2] Specifications for Abrams-Harder test may be had on request from the Portland Cement Association, 111 West Washington Street, Chicago.

another. Improper placing means the employment of such methods in depositing as will cause a separation of the mortar from the coarse aggregate, or rather segregation of the coarse material and thus annul the results of perfect mixing. Any method which allows the coarse aggregate to come tumbling into the forms with only a coating of mortar should not be used for watertight concrete construction. The use of an excess of water is almost sure to result in separation of the coarse aggregate from the mortar. A perfect mix can not be obtained even in a mixer when a large excess of water is used, and it is next to impossible to get a soupy mix into the forms without producing further imperfection in the homogeneity of the mixture. Furthermore, if it were possible to get a soupy mixture into the forms without segregation, a porous concrete would be almost sure to result, because water in excess of that required for complete hydration of the cement occupies space, which will be left vacant when the excess water escapes.

Density, in the popular sense of having no large continuous or connected voids, should always be the first consideration for containers of liquids, but it has an added importance in connection with certain chemicals. The walls of a concrete tank may be penetrable by the contained fluid, but not pervious to it—that is, the liquid may penetrate the concrete, but not pass through it. If the liquid is neutral with respect to the concrete and remains in the liquid state at all times, no harm to the concrete will result; but if the liquid crystallizes in the pores with increase in volume, damage may result. If the liquid has chemical affinity for any of the substances, disintegration will follow. The safest general rule is to have the concrete as dense and impervious as possible.

In the construction of liquid containers the concrete should be mixed thoroughly for the full time recommended, and the placing of concrete for footings and floor, for walls, for columns, if any, and for roof should proceed as a continuous operation in each case to eliminate seams. The concrete of the walls should be well bonded to that of the floor, and when a joint is necessary, it should be sealed with a metal dam to prevent leakage at this point. Thorough spading of the concrete as placed in the wall forms is essential.

The cement should meet the requirements of the current standard specifications for Portland cement of the American Society for Testing Materials. It should be stored on the work in a weather-

tight structure with floor raised not less than one foot from the ground. Cement that has hardened or partially set should not be used.

Fine aggregate should consist of natural sand or screenings from hard, tough crushed rock or pebbles, clean and free from any surface film or coating. It should be well graded from fine to coarse particles, passing, when dry, a screen having four (4) meshes to the linear inch. Fine aggregate should not contain injurious vegetable or other organic matter as indicated by the Colorimetric Test,[3] or more than seven (7) per cent by volume of clay or loam. If there is more than seven (7) per cent in one (1) hour's settlement, after shaking a sample in a one hundred (100) per cent excess of water, the material represented by the sample should not be used.

Coarse aggregate should consist of clean, durable crushed rock or pebbles, graded in size, free from vegetable or other organic matter, and should be practically free from soft, flat, or elongated particles. It should not be chemically reactive with the liquid to be contained. It should be well graded from one (1) inch down, not more than five (5) per cent passing a screen having four (4) meshes per linear inch. For tank walls more than ten (10) inches in thickness the maximum size of aggregate may be one and one-half (1½) inches. For walls less than six (6) inches the maximum size of aggregate should be three-quarters (¾) inch. Aggregate containing frost or lumps of frozen materials should never be used.

Crusher-run stone, bank-run gravel, or mixtures of fine and coarse aggregate, prepared before delivery on the work, should not be used, because the ratio of fine to coarse material varies so widely as to prevent securing a concrete mixture of uniform proportions. It is almost impossible to transport and handle pre-mixed aggregate without " ravelling out," that is, separation of the fine and coarse aggregate.

Water should be free from oil, acid, and injurious amounts of vegetable matter, alkali or other salts. Water that is drinkable is safe for concrete work.

Reinforcing metal should meet the requirements of the current standard specifications for steel reinforcement of the American Society for Testing Materials. Either plain or deformed steel bars or wire mesh may be used. When deformed bars or wire mesh are used,

[3] Abrams-Harder test for organic impurities in sand.

they should have a net cross-sectional area equivalent to that of plain bars.

Reinforcing metal should be free from excessive rust, scale, paint, or coatings of any character which would tend to reduce or destroy the bond, and should be so stored and cared for at the work as to insure its being placed in the structure in a clean condition.

The unit of measure should be the cubic foot. Ninety-four (94) pounds (one sack or one-fourth barrel) of cement should be assumed as one cubic foot.

The concrete should be mixed in the proportion by volume of not less than one (1) sack of Portland cement, not more than one and one-half (1½) cubic feet of fine aggregate, and not more than three (3) cubic feet of coarse aggregate.

The method of measuring the materials, including water for the concrete or mortar, should be one which will insure separate and uniform proportions of each of the materials at all times. Uniformity of proportions for the aggregates can best be maintained by the use of bottomless measuring boxes or of wheelbarrows whose capacities have been carefully predetermined.

All concrete should be mixed by machine (except when under special conditions the engineer permits otherwise) in a batch mixer of an approved type, preferably equipped with suitable charging hopper, water storage, and a water measuring device which can be locked.

The ingredients of the concrete should be mixed to the required consistency and the mixing continued not less than one and one-half (1½) minutes after all materials are in the mixer and before any part of the batch is discharged. The mixer should be emptied before receiving materials for the succeeding batch. The volume of the mixed material used per batch should not exceed the manufacturer's rated capacity for the drum.

The quantity of water used in mixing should be the least that will produce a plastic or workable mixture which can be worked into the forms and around the reinforcement. Not more than six (6) gallons of water should be used per bag of cement for the proportions specified unless the narrowness of the space and closeness of the reinforcement requires a wetter mix to obtain perfect filling of the forms and embedment of the reinforcement. With each additional volume of water added an equal volume of cement should be added, so as to preserve constant the ratio between the water and the cement. Under

no circumstances should the consistency of the concrete be such as to permit a separation of the coarse aggregate from the mortar in handling. An increase in the water cement ratio should not be permitted, as it seriously affects the strength of the concrete, and any batch containing such an increase should be rejected. Preservation of the strength and density of the concrete with the addition of more water can only be assured by the addition of a like amount of cement. The water cement ratio is the governing factor in the proportioning of given materials for best results and when this ratio has once been established it must be maintained.

When it is necessary to mix mortar by hand the materials should be mixed dry on a watertight platform until the mixture is of uniform color, the required amount of water added, and the mixing continued until the concrete is of a uniform consistency and character throughout.

Wood forms should be tight, strongly made, and firmly held in place. Metal forms should have sufficient strength to prevent warping out of shape. If forms are to be reused, they should be thoroughly cleaned. (A slush mixture of one-half petrolatum and one-half kerosene makes a good mixture for oiling forms.) The use of bolts, wires, or pipe separators through the concrete should be prohibited. Spreaders should be removed as placing of concrete progresses.

The forms should not be removed until the concrete has sufficiently hardened so that no deflection or damage will result. In warm weather column and wall forms should remain undisturbed for at least forty-eight (48) hours and roof forms at least seven (7) days. In cold weather no predetermined rules can be made.[4] If all the materials are heated and the concrete kept at or above 55 degrees for five (5) days, the concrete will be self-supporting. A slight freezing of the surface concrete may not be injurious, providing this occurs but once and the concrete is promptly thawed out and kept warm in the presence of moisture until thoroughly hardened.

The use of sliding forms may be permitted provided the forms do not expose the concrete until it has hardened sufficiently to sustain the weight of the concrete above. Sliding forms represent the ideal method of constructing tall tanks, because no construction seams occur if the work is carried on continuously.

[4] See "Concrete Work in Cold Weather" published by the Portland Cement Association.

Reinforcing steel should be bent or curved true to template, and securely wired or fastened in place, well in advance of the concreting. No lap splice should be less than forty (40) diameters. No two laps of adjacent rods should be directly opposite each other in circular walls. Splices should not be made at points of maximum stress. Clips or other methods of rigidly connecting the bars should be used only after pulling tests have demonstrated their effectiveness.

During depositing in the forms the concrete should be spaded continuously so as to embed the steel completely, work out entrapped air, compact the mass, and produce a dense surface.

The concrete for floor and roof should be placed in a manner to insure a smooth surface and be thoroughly worked around the reinforcement. It should be deposited in a continuous operation to the full thickness of the slab.

The influence of proper curing on the strength and density of concrete should be fully appreciated, as much of the advantage gained by careful attention to proportioning, mixing, and placing may be lost by improper curing. Exposed surfaces should be protected from sun and wind and the concrete kept thoroughly and constantly *wet* for a period of at least ten (10) days.

During cold weather the concrete at the time it is mixed and deposited in the work should have a temperature not lower than 60 degrees Fahrenheit, and suitable means should be provided to maintain this temperature for at least four (4) days thereafter and until the concrete has hardened.[5]

The design of concrete tanks involves no special knowledge of mechanics. The forces are usually accurately known from the nature of the material or liquid contained. In general the reinforcement should be distributed by the use of relatively small bars or wire mesh. Expansion and contraction should be given careful consideration if the temperature change is large. Ordinarily temperature changes can be cared for by a proper amount and arrangement of reinforcement. Pipes through tank walls should be flanged with a space about 1½" to 2" between the flange and the face of the concrete on each side of the wall. This space should be calked with litharge and glycerine or other material which will not be affected by the liquid stored.

Concrete tanks for water storage require no special surface treat-

[5] For methods of heating aggregates and mixing water and protecting the concrete see "Concrete Work in Cold Weather."

ment if the method of design and construction just outlined are carefully observed. Whether or not some special treatment is needed for tanks intended to contain oils, chemicals, and industrial liquids depends upon the character of the liquid in each case. The knowledge of the chemical engineer should be applied to such problems, and a brief discussion of them is appropriate as a guide at least to preliminary investigations.

The hydrolyzing action of water on the calcium silicates and aluminates of cement forms calcium hydroxide, hydrated crystalline aluminate, and hydrated calcium silicate. The calcium hydroxide within the mass of the concrete is in crystallized form. The theory has been advanced and fairly well sustained by experiment[6] that a skin coat of non-crystalline calcium carbonate is formed through reaction between the calcium hydroxide and carbon dioxide in the air. Many industrial liquids contain chlorides of some sort. Some of these chlorides are not reactive to the calcium carbonate, or at least not to the crystalline calcium hydroxide encountered immediately beneath the skin coat of carbonate. It can not be stated as a general rule that concrete tanks storing chloride solutions need no protective treatment, but there are a large number of untreated concrete tanks containing chlorides which have been successfully used for many years. These include pickling tanks of all sorts, salt grainers, brine and lye solutions for pickling olives, calcium chloride solutions, bleach liquors, zinc chlorides, etc. The calcium carbonate skin seems also to be effective in preventing action of some of the sulphates, especially if of low concentration.

The silicates almost never require any treatment of the containing tanks. Many of the vegetable and animal oils have also been successfully stored in untreated concrete tanks. One of the more important of these is cottonseed oil. Concrete tanks treated with water glass have proven successful for the storage of soyabean, peanut, and fish oil.

Concrete tanks, floors, vats, etc., which will be subject to the action of acids and some sulphates, will usually require a coating the nature of which will be determined largely by the construction and tempera-

[6] "Concrete in Sea Water," by Wig and Ferguson, *Engineering News Record,* Sept. and Oct., 1917 and letter to the Editor *Engineering News Record,* March 21, 1918, Technologic Paper No. 43, Bureau of Standards, Washington, D. C.

ture of the acid and whether or not the coating will be required to resist abrasion. The materials used for this purpose are bituminous compositions of various kinds.

The bituminous paints are used primarily on account of their cheapness and ease of application and give fair service on tanks or other vessels with a rather smooth wall, such as is obtained with a plaster or grout coat, and when exposed to mineral acids of low concentration. Two kinds are marketed: those made with an asphalt and those with a coal tar pitch base. For acids of the lower concentration the kind of base selected is immaterial. The efficiency of the coating depends upon its thickness and continuity. This can best be obtained by using a thin priming coat to insure a bond with the concrete surface, and when this is thoroughly dry, carefully applying a thicker coat of similar material. At least one week should elapse after the application of the last coat before filling the tank with acid.

The bituminous enamels are used where protection against relatively strong acids is desired, and when the cost of the structure justifies the extra expense of application. They can be employed both on smooth and rough walls and surfaces, and on account of their thickness, continuity of the coating is more easily obtained. They will not resist abrasion at elevated temperatures.

Bituminous enamel consists of two materials, the priming solution and the enamel proper. The priming solution consists usually of a relatively high melting point bitumen, of low susceptibility to temperature changes, dissolved in sufficient volatile solvent to give a paint of thin brushing consistency. It should dry to a tacky state in 30 minutes and should not flash below 30° C. by the Abel closed tester. The enamel proper should consist of a relatively high melting point bitumen similar to that used in the primer and a finely powdered siliceous mineral filter. The mineral filler is desirable, as it increases the resistance of the enamel to flowing and sagging at elevated temperatures, and to abrasion. The enamel is applied hot over the properly dried priming coat. The mineral filler should be resistant to hydrochloric, sulphuric, and nitric acids, and must pass a sieve the openings of which are not greater than 0.14 mm. (0.005″). (This corresponds to about 100-mesh sieve.)

The suitability of the material as a concrete coating may be judged by the following test:

Dry clean, dust-free concrete slab test pieces are coated with the

primer, and when this has dried to the tacky state the enamel is mopped on until a coating 3 to 5 mm. ($\frac{1}{8}$ to $\frac{3}{16}$″) thick is obtained. The temperature of application should not exceed 350° F., at which the enamel shall brush and spread out to a fairly smooth coating. The coating shall be unaffected except for a slight dulling when exposed in different places to the action of sulphuric acid, specific gravity 1.3 (about 40 per cent); nitric acid, specific gravity 1.22 (about 35 per cent); and hydrochloric acid, specific gravity 1.09 (about 18 per cent), for 24 hours.

For tanks below ground, or those in which the temperature never exceeds 100° F., material with a lower melting point than 350° F. made from a softer bitumen may be used on account of its greater ease of application.

Untreated and uncovered concrete floors not subject to acids or disintegrative chemicals will withstand very heavy traffic when properly constructed.[7]

The bituminous mastics are used for acid protection of floors on account of the thickness of the layer which must be applied, but they can be used for tanks or vats if proper care is taken in the application. They are of two kinds, depending on whether they are to be applied hot or cold.

Where a thin surfacing for concrete floors is desired, cold mastic is ordinarily used. This consists of two compositions, the priming solution and the body coat or mastic. The primer consists of a hard asphalt dissolved in a volatile solvent to a fairly thin brushing consistency. The mastic consists of the primer into which sufficient asbestos and finely powdered siliceous material fillers are ground so as to obtain a very thick pasty fibrous mass. Occasionally a finishing coat is applied where a color other than black is desired. In that case pigments are added to the last coat of the mastic. The method of application is as follows: The smooth concrete surface is thoroughly dried and cleaned of all grease and dust. The priming coat is then applied, and when it has dried to the tacky state a thin layer, about $\frac{1}{32}$″, of the mastic is trowelled on. When this has dried successive $\frac{1}{32}$″ coats of the mastic are applied until the required thickness is obtained.

The hot mastics are somewhat similar to the mixtures used in

[7] See Proposed Standard Specifications for Concrete Floors. American Concrete Institute. Copy on request to the Portland Cement Association.

laying sheet asphalt pavements. However, they contain a little more asphaltic binder, so that when they are heated to the temperature where the asphalt is fluid they can be poured and trowelled into place. They are satisfactory only when applied in layers one inch or more in thickness. When mixed and ready for laying, they consist of about 15 per cent of asphaltic binder, about 20 per cent of finely powdered siliceous mineral filler, 85 per cent of which will pass a 100-mesh screen, and the remainder properly graded sand or other aggregate, containing no particles larger than those passing a ¼-inch sieve. The proper grading of the aggregate so as to get a composition having a maximum density is very important, as upon it the stability and efficiency of the floor covering largely depends. The thoroughness with which the materials are mixed and the care with which they are laid also contribute to the life of the finished surface.

Hot mastics have given satisfactory service in a wide variety of chemical and dye manufacturing plants, plating acid tanks, storage-battery rooms, the pulp rooms of paper mills, and in the leaching tanks of copper and gold refineries.

As mentioned above, one of the prime requisites of liquid containers is density. In fact, there is evidence that the action on concrete of certain chemicals and even acids of certain concentrations is inversely as the density of the contact surface. Gunite, which is cement, sand and water, shot into place under air pressure with a cement gun, is very dense and has been successfully used for an acid house roof, to repair steel sulphide tanks, to line ammonia tanks, to line dens used in the preparation of fertilizers, etc. Gunite has also proved satisfactory as a lining for sulphuric acid tanks and for acid "pickling" tanks for castings.

Investigators are in essential agreement that the quality of the concrete has a marked effect on its ability to withstand practically all disintegrating agencies. It, therefore, seems appropriate to close this paper with the statement that for concrete in chemical works, whether or not surface coatings, integral compounds, surface hardeners, or any of the multitude of preparations widely advertised are used, there is nothing that will compensate for neglect to follow implicitly those methods and practices which have been found in both laboratory and field to produce the highest quality of concrete.

Discussion

President Howard: This paper is open for discussion.

Mr. Crosby Field: Mr. Chairman, following Mr. Irwin's lead, on gunite, I desire to invite the attention of the members to a rather cheap construction which has proven advantageous for us in several cases.

First, in your chemical building, put up the cheapest sort of wood structure, and after the experiments with the process are finished, which will take from five months to fifty years, just run a metal lathing or wire screen on the inside framework of the building and go after it with a cement gun. The cost varies from 50 per cent to 66 per cent of the cost of tile or any other method, and when that is done you have a good foundation and the thinnest wall that is fireproof, and you have a perfect building. You can recommend that as having been tried successfully. The same thing applies to the lengthening of life of ordinary vats. When your wooden vat gets too rotten to hold the fluid it contains, go after it with a gun and you have a new tank. From running tests between gunite tanks and tanks with very thorough hand-tamping for use in acids, we have been unable to prove any difference between the gunite and the hand-tamping, although we believe the gunite to be somewhat superior. Only time can settle that question definitely.

Mr. Irwin: The cement gun furnishes a very convenient method of obtaining a thin, dense, reinforced coating on a wall. There are other machines which have been developed for placing stucco, but I have no information about the use of these machines to construct enclosing or partition walls in buildings, or to line tanks. I have seen a great deal of gunite wall, and I think there is a large field for the use of the cement gun in chemical plants and in the construction of enclosing and partition walls in large buildings.

Mr. Field: I don't know that I made it clear that the gun could be applied without change in frame or apparatus. All you need is provision to keep the "splash" out of the places where you don't want it to stay.

Mr. Wadsworth: I should like to ask about gunite machines. I had some experience five or six years ago with the older type of gunite and the results were very uneven. I remember two buildings that were in excellent condition and another building that was pretty rotten, and a tank that was terrible. We could not seem to coat it

with those old machines, and I wondered whether improvements had made possible a more even coating.

MR. IRWIN: I think I can answer that with certainty, and my friend [indicating Mr. Field] can also doubtless answer it in the same vein. A skilled operator will produce a surface that is everywhere dense and with fairly even thickness. The surface can also be darbied or otherwise treated for appearance. There are sometimes sand streaks, but these are due for the most part to imperfect manipulation by the nozzle man. The cement gun equipment has been improved in late years to such mechanical perfection that it may be said that all the "bugs" have been worked out of it.

DR. WITHROW: I imagine that the success of a great deal of this concrete work is dependent on the effect of chemical action which may take place. There are other factors, too. Some substances are very leak or pore seeking. For instance, I remember a set of storage tanks for holding melted paraffin which were erected in a large match factory. They leaked paraffin like a sieve and were replaced by steel eventually.

MR. IRWIN: Were they lined with gunite?

DR. WITHROW: They were not lined with anything, and I wonder whether gunite would save them.

MR. IRWIN: I think you could have done something with them. The gunite lining would have decreased slightly the capacity of the tank. The old shell would furnish some strength to take care of the pressure, and the gunite lining shot on wire mesh would furnish additional support, as well as provide a dense contact surface.

MR. FIELD: Some ten years ago we were endeavoring to bring out electrical reactances, which consisted of wire imbedded in concrete molds, and in order to try various stunts to get increased capacity and impermeability we tried to permeate it with paraffin, and we found that it would not permeate.

MR. IRWIN: I believe there is much room for improvement in the ordinary practice of hand-tamping and placing of concrete. The density and strength of gunite results largely because the cement gun applies the material with force and provides a mechanical control of the amount of water used in the mix. The gun can not be operated unless a fairly constant and small amount of water is used and therein lies a great virtue. The effect of the use of one gallon more water than is necessary to produce concrete of a plastic consistency is to

reduce the strength of the concrete about as much as though two gallons of cement were left out.

PRESIDENT HOWARD: What do you think of the advantage of adding a small amount of lime hydrate for waterproofing?

MR. IRWIN: Concrete of properly proportioned materials, thoroughly mixed, carefully placed and properly cured, will be watertight under ordinary conditions. The reduction in the strength of concrete that almost invariably results from admixtures to cement may not be considered important provided the amount of admixed material is small. The addition of hydrated lime up to ten per cent by weight of the cement is often specified, but for concrete which will be exposed to contact with chemicals careful consideration should be given to the chemical reactions that might be introduced by the admixtures.

PRESIDENT HOWARD: Is there any further discussion?

DR. WESTON: I just wanted to say that there is a preparation on the market for coating metallic iron, which will save a porous tank very often.

MR. HUFF: I should like to ask a little more about this cement-water ratio. About eight years ago I came in contact with research on this subject carried out at the Sheffield Scientific School at Yale, and at that time I understood that water in excess of the critical ratio was very undesirable in the early or green stages, but that after the mix had stood for some time and the excess water had dried out, that the mix reached a state which was very closely comparable with or practically the same as that obtained when the correct ratio had been used initially, provided the other properties are the same.

I have never heard since whether this information is correct or not and should like to know.

I should also like to ask if anyone present has had experience in the use of concrete in sodium carbonate solution?

MR. IRWIN: The excess water over that necessary to complete the hydration of the cement unquestionably reduces the ultimate strength of the concrete. Professor Abrams proved this by thousands of tests. The ultimate strength of the concrete will be inversely as the ratio of the water to cement used. To illustrate: Assume that a certain mixture using a volume of water equal to the volume of cement—that is, a water-cement ratio of unity—will produce a concrete of 2,500 pounds per square inch compression at 28 days. It

will be found that with the same amount of cement and aggregate, and with exactly the same perfection of mixing and conditions of curing, but with more water, the compressive strength at all periods will invariably be less. If, however, the amount of cement is also increased so as to keep the water-cement ratio constant, the strength will remain practically constant. In other words, greater plasticity resulting from the use of more water can be obtained without sacrifice of strength only by the addition of a corresponding quantity of cement.

The effect of sodium carbonate in solution on high quality concrete should be inappreciable. Extensive investigations of the effect of various alkalies on concrete have resulted at least in preliminary conclusions that the carbonates and chlorides are not damaging to dense, strong concrete. As I mentioned in my paper, it is quite well recognized that a skin coat of calcium carbonate is formed on a surface of concrete exposed to air during the process of hardening. This calcium carbonate acts as a protective coating and the presence of sodium carbonate in solution would seem to assist in the formation of this calcium carbonate skin rather than to cause disintegration of the concrete. More information along this line may be expected as a result of the extensive investigations now in progress of the effect of various alkalies on concrete. But, in the meantime, I feel that there would be little likelihood of disastrous results in using first-class concrete in contact with sodium carbonate in solution.

PRESIDENT HOWARD: Any further discussion?

DR. WITHROW: I think that sodium carbonate is something about which no one should base a conclusion on one or two experiments. I have two pictures in my mind regarding the use of concrete in chemical plants that perhaps could be explained, if we are governed by the facts. One is in the starch plant at Argo, Illinois, which the Institute visited, where sulphur dioxide came off above the screens which separate the starch and gluten from the steep water. The concrete beams and ceiling were strongly disintegrated where the mixture of steam and sulphur dioxide strike them.

Another case is in Columbus, Ohio, in the municipal water filtration and softening plant constructed fifteen years ago. The tanks to hold the treating solutions failed, and they leak at the present time. No one can say why that was. They were to hold soda ash solution. I think if the gentleman [Mr. Huff] will look into that case he might find some interesting information.

ASBESTOS PROTECTED METAL: ITS DEVELOPMENT, MANUFACTURE AND USES

By JAMES H. YOUNG[1]

Read at the Richmond Meeting, December 7, 1922

General History of Asbestos Protected Metal

Starting in 1905, at Canton, Mass., with an idea that a steel sheet could be protected from corrosion by dipping it in molten asphalt, and then pressing a layer of asbestos felt on each side of the coated steel to protect the asphalt, Mr. H. H. Robertson stuck by this idea

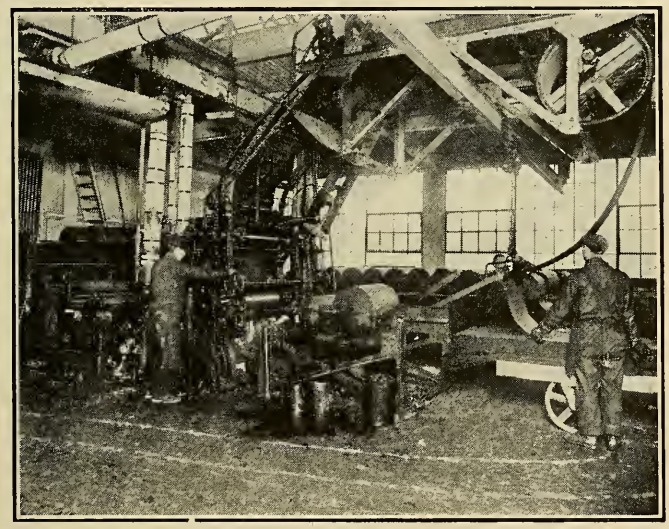


Fig. 1. The So-called Felting Machine in Operation. The steel sheets travel through hot asphalt and upward through combining rolls which press asbestos felt on to both sides of the steel sheet and fold the edges of the felt around the steel, forming a continuous web.

until the present product was evolved. The original product was a failure, the asbestos felt rapidly washing from the sheet upon ex-

[1] Senior Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

posure and collecting in the roof gutters or on the ground. To overcome this difficulty the asbestos felt was saturated with a waterproofing mixture, of which China wood oil was the principal ingredient. The resultant product was an improvement over the original material and really gave pretty good service. However, the edges and ends of the steel sheet were unprotected, which resulted in a weakness which was finally overcome by folding the felt over the edges of the steel. Commercial success was not achieved until 1909, when new machinery was developed by the late Dr. E. T. Newsome,

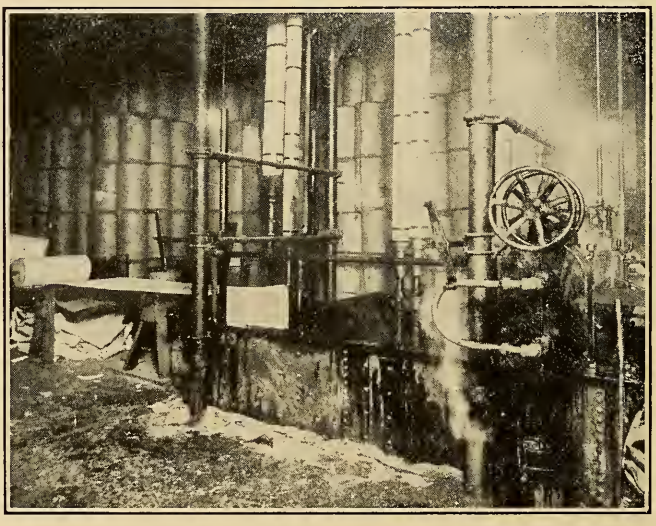


FIG. 2. Saturating Asbestos Felt.

which made it possible to manufacture a product consisting of a sheet-steel core covered with asphalt and wrapped in asbestos felt saturated with a waterproofing agent. This product of 1909, although possessing sufficient merit to warrant its being sold, was considered far from perfect. It may be added, though, that there are a number of installations of this 1909 product which still are serviceable.

Recognizing that improvements were possible in its product, the manufacturing company adopted the policy, still adhered to, of utilizing a part of its resources each year in development work. As a result of the researches carried out during the period 1909–1916, the present product was worked out and produced in 1916. The present

product differs from that of 1909 in that asphalt is used to saturate the asbestos felt and the felt layer itself is protected by a bituminous coating which retards the drying and hardening of the bituminous layers beneath, thus increasing greatly its weather-resisting properties.

The original asbestos protected metal was made in Canton, Mass. In 1911 the company moved to Beaver Falls, Pa., and in 1916 the present factory at Ambridge, Pa., was occupied.

Requisites of Roofing and Siding Materials

Before taking up in detail a discussion of "Asbestos Protected Metal," it seems appropriate to list the essentials of the perfect roofing and siding material. When a roofing and siding material is referred to, there is meant the type represented, for instance, by corru-

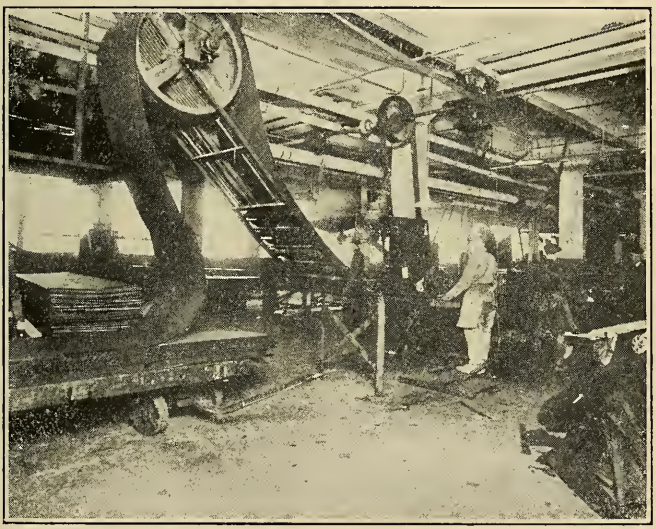


Fig. 3. Cutting the Continuous Web into Individual Sheets.

gated galvanized iron which is used to cover the so-called "skeleton type" building.

It is believed that the perfect roofing and siding material, in order to meet various and complex requirements of roofing service, should have the following characteristics: (1) It should have strength; (2) it should be resistant to weathering; (3) it should be light in weight;

(4) it should be adaptable to buildings of standard design; (5) it should have a low fire hazard; (6) it should have a low thermal conductivity; (7) it should be capable of being made to conform to any color scheme required; and, finally (8), it should have a reasonable first cost and a low per year cost.

The Characteristics of "Asbestos Protected Metal"

Since steel is the basis of "Asbestos Protected Metal," the strength requirement is well taken care of. By choosing steel of the proper gage, "Asbestos Protected Metal" may be made to span successfully

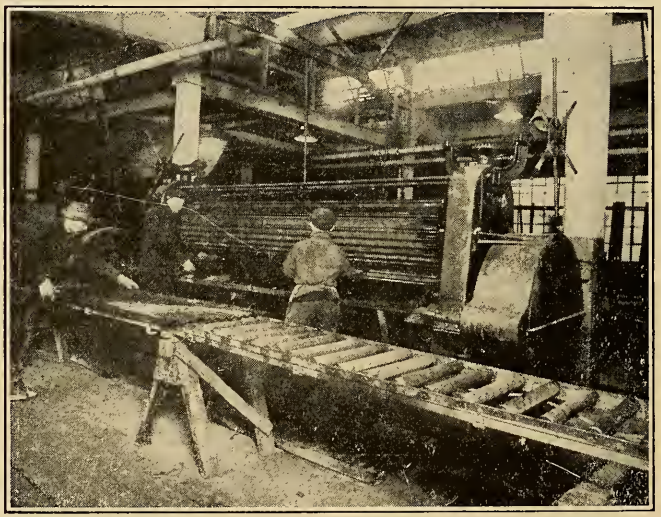


Fig. 4. The Other Side of the Corrugating Machine.

any purlin spacing ordinarily used. The weight of asbestos protected metal is approximately 1.3 times that of galvanized iron. Being similar in form, strength, and weight to ordinary corrugated steel roofing, it can be applied like corrugated steel, and may be worked into flashings and other standard shapes. It is easily adaptable to the general run of mill buildings, without the necessity of designing the buildings to meet any limitations of the roofing material.

In order to get a better idea of the durability of "Asbestos Protected Metal," it is desirable to describe the various protective coat-

ings used over the steel and the methods of applying them. The first and most important bituminous coating is applied by pulling the clean steel sheet through a vat of asphalt maintained at a temperature of 350° F. The viscosity of the asphalt at this temperature is such that a uniform coating weighing about 16 pounds per square (100 sq.ft.) is put on the steel. As the coated steel emerges from this tank, asbestos felt, previously saturated with asphalt, is pressed on to both sides and folded around the edges of the steel, thus completely sealing it. The next operation consists of running the so-called felted sheets

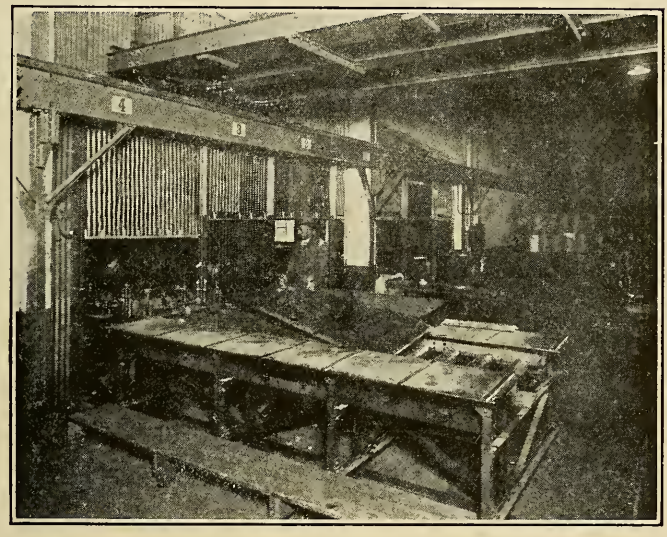


FIG. 5. Feeding Steel Sheets into the So-called Felting Machine.

through coating rolls, which apply the top waterproofing coat. The coating rolls operate at a temperature of about 425° F. The whole process is one in which no solvents are used, the asphalts being applied in a melted condition.

The asphalt used directly on the steel is an air-blown petroleum asphalt having a low susceptibility factor, soft and adhesive at low temperatures, yet not flowing at temperatures reached on roofs, even in the tropics. It contains practically no mineral matter and is chemically quite inert, particularly toward acids and slightly less so toward alkalies.

The saturant for the asbestos felt is also an air-blown asphalt of the asphalt-base petroleum type, and it, also, is quite inert chemically.

The top or weather-proofing coating is a compounded bitumen, being of the so-called stearin-pitch type. It is similar in composition to the best baking japan bases and withstands weathering conditions very well.

"Asbestos Protected Metal" thus has three layers, each of which is of bituminous composition of substantial thickness. The chemical nature of these compositions is such that they will resist a wide range of chemical conditions. Asphalt will resist the chemical action of a

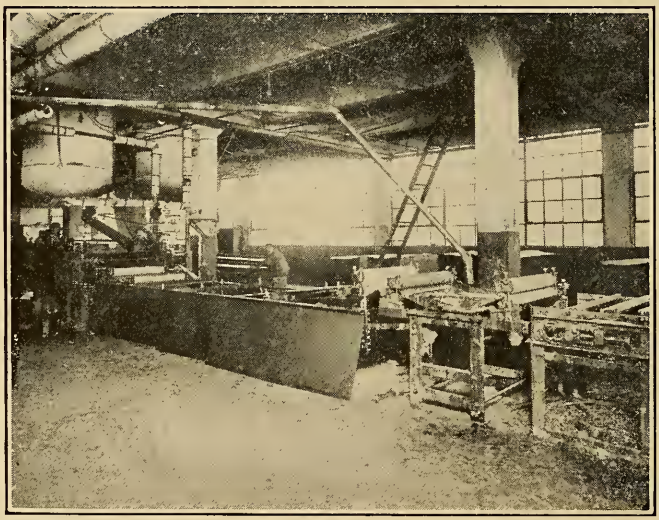


FIG. 6. The Other side of the Coating Machine. Showing cooling tank for cooling the asphalt coating and the tank for applying the solution of cellulose-thio-carbonate.

wider range of chemicals than any other commercial adhesive known at present. A study of the performance of "Asbestos Protected Metal" under actual service conditions of all sorts and in all climates shows that it is a relatively durable building material.

Regarding the fire hazard of "Asbestos Protected Metal," since each square of metal has approximately 36 pounds of asphalt on it, there is a certain fire hazard involved in its use. Where used on a roof, the hazard is of little consequence, because burning embers and

the like, falling on such a roof, will fail to produce a spreading fire. In other words, the asphalt has such a low combustion rate that the heat is dissipated upward too rapidly to keep the film burning and the fire is localized at the spot where the ember falls. In case of a side wall a fair-sized fire at the base may ignite the coating, and under favorable conditions it will continue to burn upward until the roof is reached.

While the fire hazard of a roofing and siding material is an important factor to be considered, it is interesting to note that the loss from corrosion is several times as large each year as the loss from fire. One gains much food for thought in looking over the long list

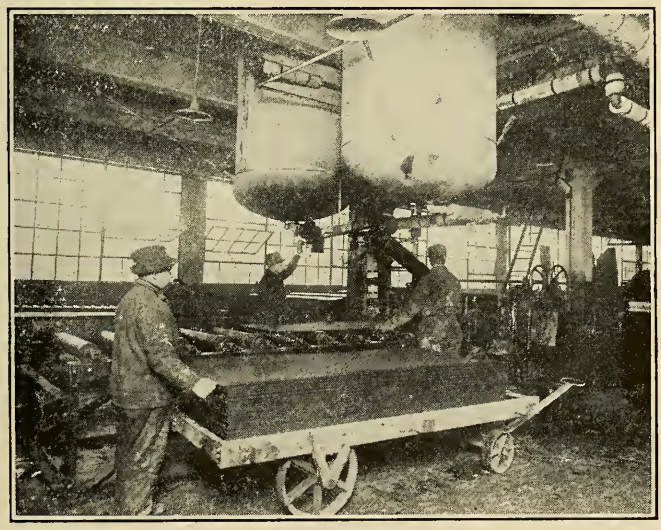


Fig. 7. Starting the So-called Felted Sheets Through the Coating Rolls Which Put on the Weatherproofing Coat.

of so-called fireproof buildings which have burned each year. Truly the fire hazard is important, but the corrosion hazard is of equal if not greater importance.

In general, it is quite important to have a roofing and siding material with a low thermal conductivity, because a building housed with such material is heated with less expense in the winter and is cooler in the summer; and also because it transmits sound less readily, as a rule. Asphalt is among the very best non-conductors of heat and it

is safe to say that "Asbestos Protected Metal" is as poor a conductor of heat as any material of equal thickness used for roofing and siding purposes. Its deficiency lies in the fact that it is not very thick; but, in actual practice, it compares very favorably with 7/8-inch pine wood insofar as heat loss is concerned.

Coming now to the subject of painting "Asbestos Protected Metal" or producing various color effects on it, it must be confessed that, outside of dark colors, such as maroon, dark green, and brown, it has been impossible to produce colors satisfactorily on it, either by painting or by incorporating pigments in its outside coating. White or light-colored drying oil paints or enamels, when used over bitumi-

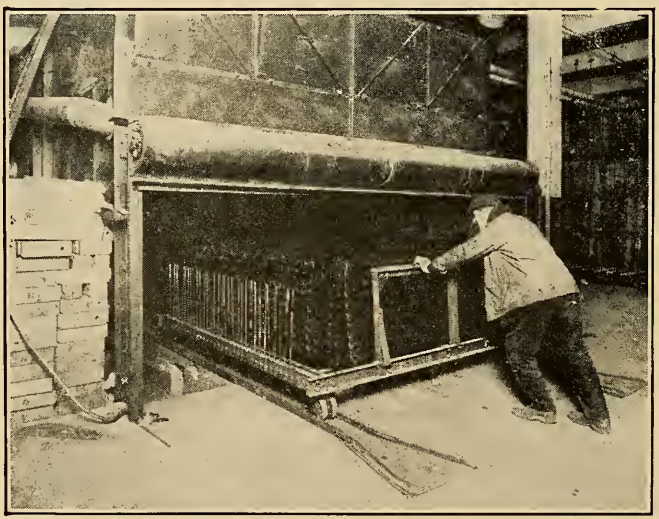


FIG. 8. Drying the cellulose-thio-carbonate solution to produce the film of cellulose-hydrate on the surface of the asbestos rotected metal.

nous surfaces, become discolored by dissolving the dark bituminous coating; then, too, the paint films tend to distort the underlying bituminous material, producing an effect commonly termed "alligatoring." If a priming coat of shellac or other similar gum is applied to a bituminous surface, a drying oil paint may then be put on without becoming discolored; but, upon exposure, cracking and "alligatoring" take place. For interior finishes a fairly satisfactory result is obtained by the shellac printing-coat method, provided either a cold-water paint

or a drying-oil paint is used over the shellac. A Manila copal spirit varnish may also be used as a priming coat. A cellulose nitrate lacquer has been developed in which alcohol is the principal component of the solvent. This lacquer is satisfactory as a priming material, and with aluminum or bronze powder it will produce a satisfactory light and heat-reflecting finish that weathers fairly well, without cracking or distorting the coating. It may be seen that, although it is possible to produce several light color effects on "Asbestos Protected Metal," they are all more or less makeshifts. It is true, however, that, on the vast majority of buildings of the type covered by materials similar to "Asbestos Protected Metal," dark colors are not objectionable; indeed, they are often preferred.

Taking up finally the factor of cost, it may be said that "Asbestos Protected Metal" compares very favorably in first cost and in per year cost with any material used for the same purpose. Erected, it costs from one and one-half to two times as much as painted galvanized iron; but on a per year basis the cost will average very much below that of painted galvanized iron, when its low maintenance cost is considered.

Summarizing the characteristics of "Asbestos Protected Metal," it may be stated that it is strong, durable, adaptable and light in weight, and has a fairly low thermal conductivity. It has a certain fire hazard, and is not capable of being painted satisfactorily with drying-oil paints. It has a relatively low first cost and a low per year cost.

Research Problems

In the development of any industry it is natural to expect a variety of problems to arise. One such problem appeared at the time the present type of "Asbestos Protected Metal" was first marketed. It was found that, even though a very high melting-point asphalt had been used as the top weather-proof coating, the "Asbestos Protected Metal" sheets, when piled flat and shipped to southern and even northern points, would stick together firmly. All sorts of fine powders were used as surfacing materials in an attempt to eliminate the difficulty, but with little success. Research finally developed a viscose solution which could be used to coat the sheets and this worked successfully.

Another problem which has received quite a little research atten-

tion has been the fire hazard of the product. This problem has finally been solved and the product has been accepted as equal to steel sheets as a fire risk in factories by insurance companies. This result has been obtained by using asphalt containing hexachlorinated naphthalene as the saturant for the asbestos felt. It is found that when a sheet thus treated is exposed to a fire the non-combustible vapors of the chlorinated naphthalene dilute the vapors of the asphalt to such an extent that the whole will not support combustion, and consequently a fire is localized insofar as the "Asbestos Protected Metal" is concerned.

Another problem to which has been devoted much time and work is the painting of bituminous surfaces, and, as has been pointed out, its solution is not yet at hand. One very interesting development has been that of coating such surfaces with various metal films. This may be accomplished either by electroplating the surface of the asphalt or by spraying molten metal thereon. Although this work is very much in the developmental stage, hopes are entertained for its successful future. The product of this procedure may be varied so as to meet different chemical conditions; for example, the lead-coated product will undoubtedly give excellent service under conditions in which oxides of sulphur are the corrosive agents. The zinc-coated product is of pleasing appearance, and any of the metallized surfaces may be painted over satisfactorily with any drying-oil paint. Such products are easily handled, stored and shipped, and are admirably adapted to tropical use. Another interesting product results from the use of granulated slate or minerals of different colors as an outside surfacing material to produce different color effects.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH OF THE UNIVERSITY OF PITTSBURGH,
PITTSBURGH, PA.,
December 15, 1922

AN EXTENSION OF THE THEORY OF GAS-ABSORPTION TOWERS

By W. B. VAN ARSDEL

Read at the Richmond Meeting, December 7, 1922

During the past five years the attention of chemical engineers has been increasingly directed to the critical study of various fundamental unit-processes. The recent work on filtration, evaporation, drying, and distillation is representative of this new emphasis, and it seems especially significant because it corresponds to an important phase in the development of other branches of engineering. Long after the basic principles of design were known, there remained areas dedicated to "best judgment" alone—problems whose direct solution seemed so complicated or so obscure that a good guess was a more promising mode of attack. Of this nature were most of the questions on the flow of liquids, on the electrical characteristics of telephone circuits, and on the occurrence of dynamic unbalance and vibration in machines. At a later period such problems were taken from the rule-of-thumb class, precise methods of analysis having been developed. The operations which characterize chemical engineering seem to be going through just such a period of development.

An outstanding example of a unit-process whose apparatus is designed by judgment and experience alone is gas-absorption or gas-scrubbing. The basic principles of the process were laid down by Hurter[1] more than thirty years ago, but their application continued for many years to be qualitative rather than quantitative, partly, it is true, because of lack of experimental data, but undoubtedly also because of the apparent complexity of the events in the apparatus and doubt as to how any pertinent constants could be sorted out of the mass of variables. Lunge's comments[2] on Hurter's work are a good example of the way in which plant designers viewed gas-absorption. An article by Heinz,[3] appearing only eight years ago, was written

[1] Hurter, *J. Soc. Chem. Ind.*, 4, 639 (1885); 6, 707 (1887); 8, 861 (1889); 12, 226, 417, 990 (1893).

[2] Lunge, "Sulfuric Acid and Alkali," 312–30, 379 ff. (1909).

[3] R. Heinz, "Absorption and Reaction Towers for the Chemical Industry," *Z. angew. Chem.*, 26, Aufs. 419–21 (1913).

from the same viewpoint; attention was directed almost exclusively to the design of the packing-material, and the only other suggestion that could be made was that "experience shows" that 16 meters per minute is the best gas-velocity in a tower. Since 1919 the growth of interest in unit-processes has been reflected in the appearance of much more work on absorption towers. In that year Zeisberg[4] published his data on the resistance of various styles of tower-packing to gas-flow, and Partington and Parker,[5] in England, developed the theory of nitric acid absorption towers and calculated from experimental data many of the constants necessary for design. In the following year E. M. Baker[6] illustrated certain principles of gaseous absorption by data on an ammonia scrubber, and Donnan and Masson[7] established by theoretical analysis the basis of the old qualitative rules of good practice. In the interests of simplicity, however, they assumed that temperatures and gas-volumes were constant throughout the system, thus limiting to a very considerable extent the applicability of their results. Since that time a number of papers have appeared on this and related subjects: Masson and McEwan,[8] for instance, assume equilibrium attained throughout a solvent-recovery tower and calculate the efficiency of the system by the summation of a series of finite steps; Thomas,[9] also postulating equilibrium conditions, found fair agreement with theory in the behavior of an alcohol-vapor recovery system; and W. K. Lewis, analyzing the processes of rectification[10] and distillation,[11] suggests a line of attack for certain cases of temperature- and volume-change. It must be said, however, that a

[4] F. C. Zeisberg, *Chem. Met. Eng.*, 21, 765–7 (1919).

[5] J. R. Partington and L. H. Parker, *J. Soc. Chem. Ind.*, 38, 76–80T (1919).

[6] E. M. Baker, "Absorption of Gases in Spray Systems and Towers," *Chem. Met. Eng.*, 22, 122–4 (1920).

[7] F. C. Donnan and I. Masson, "Theory of Gas-Scrubbing Towers with Internal Packing," (*a*) *J. Soc. Chem. Ind.*, 39, 236–41T; (*b*) *Chem. Met. Eng.*, 23, 1115–6 (1920).

[8] I. Masson and T. L. McEwan, "Recovery of Solvent Vapors from Air," *J. Soc. Chem. Ind.*, 40, 32T (1921).

[9] R. Thomas, "Recovery of Alcohol-Vapor from Air," *J. Soc. Chem. Ind.*, 41, 34T (1922.)

[10] W. K. Lewis, "Efficiency and Design of Rectifying Columns for Binary Mixtures," *J. Ind. Eng. Chem.*, 14, 492 (1922).

[11] W. K. Lewis, "Evaporation of a Liquid into a Gas," *Mech. Eng.*, 44, 445 (1922).

very wide field of theory and experimentation remains to be explored before the design of absorption-towers becomes as definite a matter as that of say, steel structures.

Scope of Work

This laboratory has under way a systematic investigation of the technical process of dissolving a gas—specifically, sulphur dioxide—in a liquid; it is hoped that the results will be directly applicable to the design of full-size plant, and hence the experimental work must be oriented with respect to plant conditions. Operation must be at least semi-continuous, so that obviously the counter-current absorption-tower will receive the major portion of our attention; the experimental towers must be large enough so that actual commercial packing of various types may be used; and concentrations, velocities, and temperatures must cover the range which those variables do cover in practice. Several years will probably elapse before this program can be completed. Preliminary to the experimental work, however, the theory of the counter-current gas-absorption tower has been somewhat extended so as to provide a pigeon-hole for practically every type of experimental case which will arise; without such extended facilities it would be quite impossible to translate the raw data into generalizations immediately available to the designer. Previous discussions of this theory, for instance Donnan and Masson's, have been so restricted that it is doubtful whether more than five or ten per cent of the cases arising in practice would fall within their *a priori* limitations. The aim of the present paper is to remove these limitations as completely as possible without too recklessly adding to the complication of the arithmetic involved.

The two most important variables whose existence is now to be allowed are temperature and gas-velocity. That is, we do not have an isothermal system, the solute gas is not a negligible constituent as to volume and therefore the volume may change appreciably, the heat of solution or reaction may not be negligible, and the solubility of the gas may not follow Henry's Law exactly. Certain other considerations are still ignored because they are unimportant for the specific system in which we are interested. Such would be relatively slow reactions in either the gas or the liquid phase and mutual transfer of different constituents between both phases at once; the nitric acid absorption tower and the rectifying column are examples of these two classes.

The General Problem

In general terms, therefore, the problem is the analysis of a counter-current gas-liquid system in which matter and heat energy are simultaneously interchanged. The conditions which govern these transfers separately are well known. The gaseous solute is transferred at a rate proportional to the area of contact and to the degree of *unsaturation* of the liquid in that section.[12, 13, 14] It is true that there exists some uncertainty as to the exact way in which this "unsaturation" should be formulated; the vapor-pressure laws themselves are sometimes stated in terms of mole-fractions (when derived from the thermodynamic basis) and sometimes in terms of concentrations (when based on the van t'Hoff-Nernst distribution law). The existing experimental data indicate that the relatively simple concentration terms are the better. Coste[14] postulates a rate of solution proportional to "100 minus the per cent saturation," but that is equivalent to the rate of absorption of solute minus the rate of evaporation of solute, *divided* by the rate of absorption of solute, which is certainly erroneous. In concentration terms, therefore, and using the notation adopted by Donnan and Masson,[7]

$$\text{Wt. solute transferred per minute} \propto A(km - n),$$

where $A \equiv$ area of contact,

$m \equiv$ concentration of solute in gas, grams per liter,

$n \equiv$ concentration of solute in liquid, grams per liter.

$k \equiv$ Henry constant, so that at equilibrium, $km = n$.

Heat is transferred, according to Newton's law of cooling, at a rate proportional to the area of contact and to the temperature-difference between the two phases in that section,

$$\text{Heat transferred per minute} \propto A(T - t),$$

where $T \equiv$ temperature of the gas, ° C.

$t \equiv$ temperature of the liquid, ° C.

[12] Adeney and Becker, "Determination of Rate of Solution of Atmospheric Nitrogen and Oxygen by Water," *Proc. Roy. Dublin Soc.*, 15 (N.S.), 385, 609 (1918–9).

[13] Ch. Bohr, "Invasions, Evasions und Absorptions-Koefficienten von CO_2 in Wasser und Wässeriger NaCl-Lösungen," *Wied. Ann.*, 68, 500 (1899), 69, 244 (1899).

[14] J. H. Coste, "Absorption of Atmospheric Gases by Water," *J. Soc. Chem. Ind.*, 36, 846–53 (1917).

Now since $(km - n)$ and $(T - t)$ are variable from point to point in the system, the element of area must obviously be a differential one, or if the whole area of contact be taken the two potential-factors must be space-averages over this entire area. Taking the latter standpoint, and assuming that the change in volume of solution is negligible, the following equations may be written:

$$\text{Wt. solute transferred per minute}^{7} = k_1 S h k_2 (km - n)_{av.}, \quad (1)$$

where $k_1 \equiv$ surface of contact per cubic foot of gross tower-volume, square feet,

$S \equiv$ cross-section area of tower, square feet,

$h \equiv$ height of packed portion of tower, feet,

$k_1 Sh =$ total area of contact.

$k_2 \equiv$ solute transfer-coefficient, grams per minute per square foot per gram-per-liter average concentration-deficit.*

$$\text{Heat transferred per minute} = k_1 S h k_3 (T - t)_{av.} \quad (2)$$

where $k_3 \equiv$ heat transfer-coefficient, calories per minute per square foot per degree C. average temperature-difference.

The first point of fundamental difference from the ordinary heat-interchanger now arises. Instead of a constant velocity of both fluids being maintained through the entire system, one of them, the gas, constantly decreases in velocity due to the absorption of solute from it. Now both transfer-coefficients are, as an experimental fact, affected by changes in gas-velocity, and therefore if equations analogous to (1) and (2) be written for the general section of differential thickness the constants k_2 and k_3 must be replaced by variables which are functions of the gas-velocity at that point.

The next point of distinction from the heat exchanger is the important one of heat of reaction. With such a solute as SO_2 the heat of solution or reaction far exceeds, in many practical cases, the heat which would correspond to temperature-equalization alone. The heat-relations of the system are thus intertwined with solute-transfer in a very complex way, for it must be remembered that the

* This is a barbarous combination of units, but it is the inevitable result of our adherence to two systems of units in engineering work.

solubility of a gas in general decreases with increasing temperature, that is, k (the Henry constant) decreases, and so for a given m and n the rate of solution falls off. As a matter of fact it seems to be quite hopeless to attack this general case by direct analysis. It is too complicated.

Characteristic Constants

The performance of a given gas-absorption tower may be described in a number of different ways, of varying degrees of generality and usefulness. Four characteristics are of special value—the absorption coefficient (pounds solute absorbed per minute per square foot of contact surface) or the absorption factor (pounds absorbed per minute per cubic foot of gross tower volume),—both in Partington and Parker's nomenclature;[5] the per cent saturation of the resulting solution, based on the concentration of the gas entering the tower; the per cent removal of the solute from the gas; and the solute transfer-coefficient, k_2. The first three of these are, of course, complicated functions of the conditions under which the system operates; they may be used to describe the operation of a tower only under specified conditions of operation. The transfer-coefficient, on the other hand, like the heat transfer-coefficient of a heat interchanger, is to a measurable degree a characteristic of the tower; its variation with such conditions as temperature and fluid-velocities is relatively simple. Thus while the other three characteristics may define the operation of a projected installation, or describe that of a unit in actual service, any thorough study of tower-design must be based largely on the transfer-coefficient; the importance of Donnan and Masson's work[7] lies largely in the prominence they accord to this concept.

Experimental Determinations Required

The study of a gas-absorption tower presupposes accurate knowledge of the gas and of its solutions. The thing of first importance is the solubility of the gas in the given liquid at various partial-pressures and temperatures, or alternatively, the vapor-pressure of solutions of various concentrations at various temperatures. If the heat of solution is not known by direct determination it may be calculated from the vapor-pressure curve and the dissociation con-

stant of the dissolved gas (as say H_2SO_3). For accurate work the actual density of the gas at various pressures and temperatures, and the densities and specific heats of solutions of various concentrations and at various temperatures, should be known.

Given this necessary fundamental knowledge, the behavior of the tower can be analyzed almost without exception by determination of the end-conditions only. The data of an experimental run will ordinarily consist of the following quantitative measurements:

V_G' ≡ volume of gas entering the tower, liters per minute,
V_L' ≡ volume of liquid entering the tower, liters per minute,
c_1 ≡ fraction of solute-gas by volume in the entering gas, or
M_1 ≡ concentration of solute-gas in the entering gas, grams per liter,
c_2 ≡ fraction of solute-gas by volume in the exit-gas, or
M_2 ≡ concentration of solute-gas in the exit-gas, grams per liter.
N_1 ≡ concentration of solute in the entering liquid, grams per liter.
N_2 ≡ concentration of solute in the exit-liquid, grams per liter,
T_1 ≡ temperature of gas entering the tower, ° C.
T_2 ≡ temperature of gas leaving the tower, ° C.
t_1 ≡ temperature of liquid entering tower, ° C.
t_2 ≡ temperature of liquid leaving tower, ° C.

Calculation of Transfer-Coefficient

Two relations must be worked out preliminary to the establishment of general equations for determining the transfer-coefficient—one defining changes in gas-volume through the tower, and the other relating solute-concentration in the liquid phase to that in the gas-phase. Since the gas-volume is not constant, the latter will not be identical with Donnan and Masson's equation (7).[7]

If c be the volume-fraction of gaseous solute at any point in the tower, and m the corresponding concentration in grams per liter,

$$c = \frac{m}{d}, \tag{3}$$

where d ≡ the density of the pure solute-gas at the given temperature and pressure, in grams per liter. The volume of solute-gas

entering the tower per minute,

$$= V_G' c_1 = V_G' \frac{M_1}{d_1}.$$

The volume of inert gas entering per minute

$$= V_G' \left(1 - \frac{M_1}{d_1}\right).$$

At some other point in the tower, where the total gas-volume is V_G, the volume of inert gas passing per minute,

$$= V_G \left(1 - \frac{m}{d}\right).$$

Now this is the same in weight as the quantity entering the tower, but its volume has changed in response to changes in temperature and pressure *in the same way* (but inversely) as the density of the pure solute-gas, d, would have changed, or

$$V_G \left(1 - \frac{m}{d}\right) = V_G' \frac{d_1}{d} \left(1 - \frac{M_1}{d_1}\right),$$

$$V_G = V_G' \frac{d_1 - M_1}{d - m}. \tag{4}$$

For the special case of the change in volume through the whole tower, a quantity which occurs frequently in subsequent calculations,

$$V_G'' = V_G' \frac{d_1 - M_1}{d_2 - M_2} = V_G' \Delta, \tag{5}$$

where

$$\Delta \equiv \frac{d_1 - M_1}{d_2 - M_2}.$$

The general relation of n, the solute-concentration in the liquid, to m, solute-concentration in the gas, may now be formulated by means of a "solute balance." The condition of this balance for the section of the tower between the top and some other point is expressed by the equation,

$$V_G m - V_G'' M_2 = V_L n - V_L' N_1. \tag{6}$$

Assuming that V_L is substantially constant, and substituting (5),

$$m = \frac{d(f\Delta M_2 + n - N_1)}{f\Delta d_2 + n - N_1}, \tag{7}$$

$$n = f(d_1 - M_1)\left(\frac{m}{d - m} - \frac{M_2}{d_2 - M_2}\right) + N_1, \qquad (8)$$

where

where $f \equiv V_G'/V_L'$, "flow-ratio."

Now the general equation, similar to but not identical with Donnan and Masson's equation (3), describing solute-movement in a differential section is as follows:

$$V_L \delta n = k_1 S \phi k_2 (km - n)\delta x, \qquad (9)$$

where $x \equiv$ distance in the tower, measured down from top,

$\phi \equiv$ a variable multiplier of the transfer-coefficient.

The value of the transfer-coefficient, as pointed out above, depends on the gas- and liquid-velocities, among other things, but the average of ϕ for the whole tower is unity. All available experimental work (including some not yet published) indicates that to such a rough approximation as will serve at this point, ϕ varies directly as the gas-velocity when the flow ratio at the given point, V_G/V_L, is less than a critical value, f_c, (which appears to be approximately equal to k) and directly as the liquid velocity if the flow ratio is greater than that value, as suggested in Fig. 1; and when the temperature of the liquid changes, ϕ varies inversely as the viscosity of the liquid, η_t. The mode of variation of ϕ in the tower will evidently depend on the relation of the flow-ratio to the critical value f_c; four cases will arise, since at a given point the flow-ratio may be greater or less than f_c and the average flow-ratio throughout the tower may independently be greater or less than f_c.

	$\frac{\mathbf{V}_G}{\mathbf{V}_L} > f_c$	$\frac{\mathbf{V}_G}{\mathbf{V}_L} < f_c$
$\frac{V_G}{V_L} > f_c$	Case (*a.*) $\phi = \frac{V_L \eta_{av.}}{\mathbf{V}_L \eta_t}$	Case (*b.*) $\phi = \frac{V_L f_c \eta_{av.}}{\mathbf{V}_G \eta_t}$
$\frac{V_G}{V_L} < f_c$	Case (*c.*) $\phi = \frac{V_G \eta_{av.}}{\mathbf{V}_L f_c \eta_t}$	Case (*d.*) $\phi = \frac{V_G \eta_{av.}}{\mathbf{V}_G \eta_t}$

where $\mathbf{V}_L$, $\mathbf{V}_G$ and $\eta_{av.}$ are average values of those variables in the given case, (see Appendix for means of estimation of these values).

Now substituting in (9) the value of m from (7) and that of ϕ from this table, simplifying and solving for k_2 (assuming also V_L constant, and therefore $V_L = \mathbf{V}_L$),

$$(a)\quad k_2 = \frac{V_L}{k_1 h S \eta_{av.}} \int_{n_1}^{n_2} \frac{(f\Delta d_2 + n - N_1)\eta_t\, \delta n}{kd(f\Delta M_2 - N_1) + n(kd - f\Delta d_2 + N_1) - n^2}, \quad (10)$$

$$(b)\quad k_2 = \frac{\mathbf{V}_G}{k_1 h S f_c \eta_{av.}} \int_{n_1}^{n_2} \frac{(f\Delta d_2 + n - N_1)\eta_t\, \delta n}{kd(f\Delta M_2 - N_1) + n(kd - f\Delta d_2 + N_1) - n^2}, \quad (11)$$

$$(c)\quad k_2 = \frac{V_L f_c}{k_1 h S \eta_{av.}} \int_{n_1}^{n_2} \frac{d\eta_t\, \delta n}{kd(f\Delta M_2 - N_1) + n(kd - f\Delta d_2 + N_1) - n^2}, \quad (12)$$

$$(d)\quad k_2 = \frac{\mathbf{V}_G}{k_1 h S \eta_{av.}} \int_{n_1}^{n_2} \frac{d\eta_t\, \delta n}{kd(f\Delta M_2 - N_1) + n(kd - f\Delta d_2 + N_1) - n^2}. \quad (13)$$

Equations of this form are integrable if k, d and η_t can be assumed constant, but the arithmetical work of a step-by-step approximate integration is usually simpler and often more rapid than substitution in the complicated forms which result. If the temperature variation can somehow be connected with n, the solution-concentration, k, d and η_t may be evaluated and equations (10) to (13) become very general paths to solution.

It was admitted in an earlier paragraph that no general analytical formulation for this connection between n, t and T had been found, but fortunately there are special considerations which make such formulation unnecessary in most cases. For instance, d does not change rapidly with changes in T, and η_t does not change rapidly with t, so that fairly rough temperature-approximations suffice for them. The Henry constant, k, however, varies quite rapidly with t, which must therefore be fixed as accurately as possible. In the larger number of practical cases the heat of solution or reaction is so considerable that it quite overbalances the sensible-heat transfer, and since it is directly correlated with changes in n the problem becomes very simple; if, on the contrary, the heat-transfer far outweighs the heat of solution, another fairly simple line of attack is open; it is only when both divisions of the heat-effect are considerable that the mode of solution is not direct and accurate.

To take the first of these cases; assume first that the heat of

solution of a gram of the solute is constant at all dilutions, then if this heat is the only cause of temperature-change, t changes proportionally to n, or:

$$t = t_1 + \frac{n - N_1}{N_2 - N_1}(t_2 - t_1). \qquad (14)$$

This equation will evidently hold with some accuracy even if the heat of solution is only the *major* cause of temperature-change, say if

$$(t_2 - t_1) - 0.001H(N_2 - N_1) < 2^\circ, \qquad (15)$$

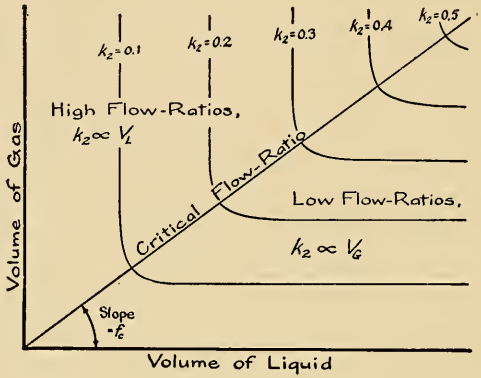
where $H \equiv$ heat of solution, calories per gram. If H varies with the concentration, as in an H_2SO_3 solution, the variation in t is, of course, not linear with respect to n, but the function being known, evaluation is possible. If the temperature-change of the gas is not too great, T may be estimated with sufficient accuracy by the same rule of linear variation with n, but if $T_1 - T_2$ is more than, say, 10° *greater* than $t_2 - t_1$, a more exact rule should be used. Now in the case of simple heat-transfer, temperature variation in one phase is proportional to that in the other phase; in our absorption system it would evidently be true that temperature-change in the gas-phase is proportional to the *excess* of temperature-change in the liquid phase above that produced by the heat of solution, provided changes in weight and specific heat of the gas-phase can be ignored. Since as stated above, T need not be carefully determined, this assumption can usually be made. Stated analytically, $T = t + (T_2 - t_1)$

$$+ \frac{(T_1 - t_2) - (T_2 - t_1)}{(t_2 - t_1) - 0.001H(N_2 - N_1)}[t - t_1 - 0.001H(n - N_1)]. \qquad (16)$$

The process of computing k_2 according to this first case therefore consists of the following steps: calculation of t by means of equation (14), for a series of assumed values of n covering the range from N_1 to N_2; calculation of T by the analogous linear relation or by equation (16); determination of the values of η_t, k and d corresponding to those just found for t and T;* summation of the computed

* If the gas in question does not follow the simple statement of Henry's law, so that k is a function of m as well as of t, m must also be determined for each value of n, by means of equation (7). The solubility data for the gas are most conveniently expressed by a graph of k against t, consisting of a family of curves for values of m ranging from zero (extrapolated) to d.

values of the function inside the integral sign of equation (10), (11), (12) or (13), and solution for k_2.



The other workable alternative, namely that in which heat of solution is far overbalanced by transferred sensible heat, may be defined by the double criterion:

$$(t_2 - t_1) - 0.001H(N_2 - N_1) > 2^\circ$$

$$\frac{0.001H(N_2 - N_1)}{t_2 - t_1} < 0.1. \qquad (17)$$

It subdivides again into two cases according as the changes in weight and specific heat of the gas-phase are or are not negligible compared to its average weight and specific heat; the case in which the change is negligible may be defined closely enough by the criterion:

$$\Delta > 0.8. \qquad (18)$$

Temperature changes under these conditions follow the well-known law characteristic of heat-exchangers, e.g.,

$$t = \frac{\dfrac{t_1(T_1 - T_2)}{t_2 - t_1} - T_2 + (T_2 - t_1)\left(\dfrac{T_1 - t_2}{T_2 - t_1}\right)^z}{\dfrac{T_1 - T_2}{t_2 - t_1} - 1}, \qquad (19)$$

where $z = x/h \equiv$ fraction of height, measured downward from top of tower. Now since gas-volume is constant, Donnan and Masson's

analysis applies, and if k be held constant for the integration, the quotient of D. and M.'s equations (10) and (11)[7] reduces to the following law of variation of n with z, analogous to equation (19) above:

$$m = \frac{(kM_2 - N_1)\left[\frac{(k-f)M_1 + fM_2 - N_1}{kM_2 - N_1}\right]^z - fM_2 + N_1}{k - f}. \quad (20)$$

The computation of k_2 evidently follows a very different course than before; the point now is to determine a *space-average* of $km - n$ which can be substituted directly in the fundamental equation (1). A series of values of z will be chosen, the corresponding t calculated by equation (19), k read from the solubility chart,* the series of values of m calculated by equation (20) and then those of n by equation (8), and the factor $(km - n)_{av.}$ computed.

The only other case which leads to a satisfactory evaluation of k_2 is the restricted one assumed by Donnan and Masson. From our viewpoint the criteria which distinguish it may be expressed as follows:†

$$\Delta > 0.8, \quad (21)$$

$$k' - k'' < 0.1k'', \quad (22)$$

where $k' \equiv$ Henry constant at top of tower,

$k'' \equiv$ Henry constant at base of tower.

Some experience with these calculations has indicated that it is by no means a matter of indifference which of the suggested forms is used; if substitution be made in their equation (11), for instance,‡

$$k_2 = \frac{V_G}{k_2 hS(k-f)} \log_e \frac{M_1(k-f) + fM_2 - N_1}{kM_2 - N_1}. \quad (22a)$$

an average value of k must be used; but any one who has calculated heat-transfer coefficients in heat-interchangers will remember that

* If k is a function of m as well as of t, reasonable values of m may be assumed at this point and the estimate checked against the values subsequently calculated.

† The criteria suggested for the various cases overlap to a certain extent; in case the choice of methods is thus presented, the simpler one will naturally be used.

‡ Solving for k_2 this equation has the following form:

in case equilibrium is nearly attained at one end, very slight temperature changes at that end correspond to disproportionately large changes in the coefficient. As a matter of fact, use of an average k may, under the proper circumstances, double or halve the true value of k_2 or even bring it out negative. The expression previously suggested by the writer [7b], avoids this difficulty:

$$(km - n)_{av.} = \frac{(k''M_1 - N_2) - (k'M_2 - N_1)}{\log_e \frac{k''M_1 - N_2}{k'M_2 - N_1}}. \qquad (23)$$

Summarizing the foregoing analysis of the calculation of k_2, the data given in any instance should first be examined so that the calculation can be classified under one of the four groups recognized:

Case 1.
$$k' - k'' > 0.1k'',$$
$$(t_2 - t_1) - 0.001H(N_2 - N_1) < 2°.$$

Case 2.
$$k' - k'' > 0.1k'',$$
$$\Delta > 0.8,$$
$$(t_2 - t_1) - 0.001H(N_2 - N_1) > 2°,$$
$$\frac{0.001H(N_2 - N_1)}{t_2 - t_1} < 0.1.$$

Case 3.
$$k' - k'' < 0.1k'',$$
$$\Delta > 0.8.$$

Case 4. All others.

The computations may be briefly outlined as follows:

Case 1. (Temperature changes in the liquid are not negligible and are due almost wholly to heat of solution or reaction.) A convenient series of values of n is chosen, covering the range from N_1 to N_2; t is calculated by equation (14) and if necessary, m by equation (7), then η_t is found from the viscosity-data for the liquid and k from the solubility-data for the gas; T is estimated by the linear rule analogous to (14) if $T_1 - T_2$ is not more than 10° greater than $t_2 - t_1$, or by equation (16) if it is more than 10° greater; d is then determined, knowing the pressure and the properties of the gas; sub-case (*a*), (*b*), (*c*) or (*d*) having been chosen according as V_G/V_L and $\mathbf{V}_G/\mathbf{V}_L$ are greater or less than f_c, k_2 is computed by summation of the function indicated by equation

(10), (11), (12) or (13). If f is only slightly greater than f_c, the flow-ratio at some point in the tower is likely to fall below f_c owing to the decrease in gas-volume; $[f(d_1 - M_1)]/(d - m)$ should be tabulated in such case, and at points beyond that of its equality with f_c, equation (12) will be used instead of equation (10), or (13) instead of (11).

Case 2. (Temperature changes in the liquid are not negligible and are due almost wholly to transfer of sensible heat; change in gas-volume negligible.) A convenient series of values of z is chosen, varying from zero to 1.0; t is calculated by equation (19) and if necessary, reasonable values of m are estimated; k is found from the solubility data, and m is calculated accurately by equation (20); n is calculated by equation (8), $km - n$ computed and averaged over the range of z from 0.0 to 1.0; k_2 is found from equation (1).

Case 3. (Temperature changes in the liquid and volume changes in the gas are negligible). The factor $(km - n)_{av.}$ is computed by equation (23) and substituted in equation (1).

Case 4. This case represents the residue of data, from which k_2 cannot be satisfactorily calculated by methods so far outlined.

Accurate Solute- and Heat-Balances

Owing to the experimental difficulty surrounding a detailed test on an absorption tower of any size, it is seldom indeed that the data secured are free from uncertainties at all points. It is therefore highly desirable to determine the consistency of the figures before proceeding too far with other calculations; the obvious way is to balance up both solute and heat. These balances may be made relatively exact by eliminating all unnecessary simplifying assumptions, and the results then indicate the reliability of the data.

When solute and heat are simultaneously transferred, the heat-balance is considerably complicated by the change in weights and specific heats of the phases, as may be understood best by thinking of a hypothetical cycle of operations: the mass of gas entering the system in unit time is cooled to some arbitrary temperature, say t_1, the heat abstracted being $W_G' s_G' (T_1 - t_1)$,

where $W_G' \equiv$ weight of gas entering, in grams, per minute,
$s_G' \equiv$ specific heat of gas entering.

At this temperature a part of the solute is removed by absorption in the liquid, but since the pressure is constant this involves no heat-effect in the gas. The new volume of gas is raised in temperature from t_1 to t_2 by an input of heat equal to $W_G''s_G''(t_1 - T_2)$,

where W_G'' ≡ weight of gas leaving, in grams, per minute,

s_G'' ≡ specific heat of gas leaving.

The liquid enters at temperature t_1 and may be assumed to increase in weight at this temperature, due to absorption of solute, with an evolution of heat equal to $H(V_L''N_2 - V_L'N_1)$; it then is raised in temperature to t_2 by a heat-input equal to $W_L''s_L''(t_1 - t_2)$. In most actual systems there will be an additional heat-effect due to evaporation of liquid into the gas, or condensation of moisture from the latter, although this has been ignored in the preceding analysis; this heat-effect will be equal to the heat of vaporization per gram, times the net weight of liquid evaporated or condensed. If the gas leaving the top of the tower is saturated, the weight of vapor carried off is $V_G''a_2$,

where a_2 ≡ density of saturated vapor at temperature T_2, in grams per liter.

The weight of vapor entering is $V_G'a_1F$,

where a_1 ≡ density of saturated vapor at temperature T_1, grams per liter.

F ≡ relative "humidity" of entering gas.

The heat-effect is therefore $L(V_G''a_2 - V_G'a_1F)$,

where L ≡ heat of vaporization of the liquid, cal. per g.

The combined heat-balance therefore becomes:

$$W_G's_G'(T_1 - t_2) - W_L''s_L''(t_2 - t_1) + W_G''s_G''(t_1 - T_2) + H(V_L''N_2 - V_L'N_1) - L(V_G''a_2 - V_G'a_1F) = 0. \quad (24)$$

This expression may be reduced to one containing only known or measured quantities when the specific nature of the system is given; for instance, for SO_2 and air,

$$W_G's_G' = 0.107V_G'(d_1 + 0.450M_1), \quad (25)$$

$$W_G''s_G'' = 0.107\Delta V_G'(d_2 + 0.450M_2). \quad (26)$$

The solute balance, in its general form is as follows:

$$V_G'M_1 - V_G''M_2 - V_L''N_2 + V_L'N_1 = 0. \quad (27)$$

The quantity V_L'' may be reduced to directly measured terms:

V_L' liters of liquid entering, weigh $1000\sigma_1 V_L'$ grams where $\sigma_1 \equiv$ density of incoming liquid, grams per cc,

V_L'' liters of solution leaving, weigh $1000\sigma_2 V_L''$ grams where $\sigma_2 \equiv$ density of outgoing liquid;

Weight of solute in liquid entering, $V_L'N_1$ grams; in liquid leaving, $V_L''N_2$ grams.

Weight of water entering is therefore $1000\sigma_1 V_L' - V_L'N_1$ grams and the same weight, leaving, is $1000\sigma_2 V_L'' - V_L''N_2$ grams.

$$V_L''(1000\sigma_2 - N_2) = V_L'(1000\sigma_1 - N_1),$$

$$V_L'' = V_L' \frac{1000\sigma_1 - N_1}{1000\sigma_2 - N_2} \tag{28}$$

The reduced form of equation (27) is therefore,

$$V_G'(M_1 - \Delta M_2) - 1000 V_L' \frac{\sigma_1 N_2 - \sigma_2 N_1}{1000\sigma_2 - N_2} = 0. \tag{29}$$

Computation of Other Characteristics

The computation of the other commonly used characteristics of an absorption system, namely the absorption coefficient (or absorption factor), the per cent removal of solute from the gas and the per cent saturation of the resulting solution, presents no difficulty in any case.

Absorption Coefficient.—Neglecting changes in liquid-volume, the coefficient (pounds solute absorbed per minute per square foot of contact-surface) is given by the following expression:

$$A.\ C. = \frac{V_L'\ (N_2 - N_1)}{453.6\ k_1 h S}. \tag{30}$$

Absorption Factor.—The absorption factor varies from the absorption coefficient only in being based upon gross tower volume, instead of on contact-surface:

$$A.\ F. = \frac{V_L'\ (N_2 - N_1)}{453.6\ hS}. \tag{31}$$

Per cent Removal of Solute from Gas.—The removal of solute from the gas is evidently equal to the ratio of the weight entering per

minute minus the weight leaving per minute, divided by the weight entering per minute:

$$r = \frac{100(V_G'M_1 - V_G''M_2)}{V_G'M_1} = \frac{100(M_1 - \Delta M_2)}{M_1} = 100\left(1 - \Delta\frac{M_2}{M_1}\right). \tag{32}$$

Per cent Saturation of Resulting Solution.—If this saturation is based upon the concentration of solute in the gas entering the system, its value is evidently:

$$\psi = \frac{100N_2}{k''M_1}. \tag{33}$$

There is an interesting and important relation between the removal of solute from the gas and the saturation of the resulting solution. Noting that equation (32) can equally well be written:

$$r = \frac{V_L(N_2 - N_1)}{V_G'M_1}$$

or

$$r = \frac{N_2 - N_1}{fM_1}$$

and combining with equation (33),

$$r = \psi\frac{k''N_2}{f(N_2 - N_1)}. \tag{34}$$

For the common case where $N_1 = 0$ this reduces to:

$$r = \psi\frac{k''}{f}. \tag{35}$$

Design of an Absorption System

The day will presumably come when there will be available to designers as accurate a body of data on solute-transfer coefficients as we now have on heat-transfer coefficients. For any given solute and solvent this tabulated material will certainly include as the independent variables, (*a*) the style and size of unit of the tower-packing, (*b*) the ratio of height to diameter in the tower, (*c*) the rate of liquid-supply per square foot of cross-section, (*d*) the rate

of gas-supply per square foot of cross-section, (*e*) the temperatures of both phases, and possibly other factors capable of modifying the transfer-coefficient. If and when such data are available, an absorption tower may be designed by nearly the same process of computation as was described above for the evaluation of transfer-coefficients.

Supposing a case of the type which will usually arise, we have given a known volume of gas, of known concentration and temperature, and from that gas we wish to remove by means of a solvent (say $N_1 = 0$) of known temperature at least $r\%$ of the solute constituent, producing a solution $\psi\%$ saturated; how large a tower is necessary if we use the X. Co.'s packing-material, how much liquid will be required and at what temperature will it emerge, and how much spent gas, of what strength, will be left? A minimum cross-section for the tower may be considered as fixed by considerations of power-requirement for forcing the gas through it, and a maximum height by structural requirements.

If T_2 be assumed equal to t_1, ΔM_2, and hence M_2, may be calculated from equation (32); $V_L N_2$ can be found from equation (29), and t_2 from (24), again assuming $T_2 = t_1$; k'' and k' can then be found, then f by equation (35), and finally V_L and N_2, since V_G' is known. The case may now be classified as described for the calculation of k_2, and the same means of solution are followed, except that the product $k_2 h S$ is to be found instead of k_2 alone. Now it may be supposed that the transfer-coefficient data show a certain ratio of S to h to be desirable; if this ratio be assumed, the quantity $k_2 S^2$ is known. The transfer-coefficient will be tabulated or plotted against V_G'/S and V_L/S; therefore consistent values of k_2 and S may be determined by inspection of this table or plot. If the result oversteps the limitations of dimension imposed by the conditions, the ratio of S to h will be modified until the conditions are met.

Symbols

The symbols used in this paper (taken as far as possible from Donnan and Masson's nomenclature) are as follows, in the order of their appearance:

$A \equiv$ Total area of phase-contact in tower, square feet,

$m \equiv$ Concentration of solute in the gas at any point, grams per liter,

$n \equiv$ Concentration of solute in the liquid at the corresponding point, grams per liter,

$k \equiv$ Henry constant, $= n/m$ at equilibrium,

$T \equiv$ Temperature of the gas at any point, ° C.,

$t \equiv$ Temperature of the liquid at the corresponding point, ° C.,

$k_1 \equiv$ Surface of contact per cubic foot of gross tower-volume, square feet,

$S \equiv$ Cross-section area of tower, square feet,

$h \equiv$ Height of packed portion of tower, feet,

$k_2 \equiv$ Solute transfer-coefficient, grams per minute per square foot per gram-per-liter average concentration-deficit,

$k_3 \equiv$ Heat transfer-coefficient, calories per minute per square foot per degree C. average temperature-difference,

$V_G' \equiv$ Volume of gas entering the tower, liters per minute,

$V_L' \equiv$ Volume of liquid entering the tower, liters per minute,

$c_1 \equiv$ Fraction of solute-gas by volume in the entering gas,

$M_1 \equiv$ Concentration of solute-gas in the entering gas, grams per liter,

$c_2 \equiv$ Fraction of solute-gas by volume in the exit-gas,

$M_2 \equiv$ Concentration of solute-gas in the exit-gas, grams per liter,

$N_1 \equiv$ Concentration of solute in the entering liquid, grams per liter,

$N_2 \equiv$ Concentration of solute in the exit-liquid, grams per liter,

$T_1 \equiv$ Temperature of gas entering the tower, ° C.,

$T_2 \equiv$ Temperature of gas leaving the tower, ° C.,

$t_1 \equiv$ Temperature of liquid entering the tower, ° C.,

$t_2 \equiv$ Temperature of liquid leaving the tower, ° C.,

$\Delta \equiv$ Ratio of volume of gas leaving the tower to the volume entering the tower,

$d_1 \equiv$ Density of the pure solute-gas at temp. and pressure prevailing at the gas-inlet, grams per liter,

$d_2 \equiv$ Density of the pure solute-gas at temp. and pressure prevailing at the gas-outlet, grams per liter,

$d \equiv$ Density of the pure solute-gas at temp. and pressure prevailing at any point in the tower, grams per liter,

$f \equiv$ Flow ratio, ratio of volume of gas entering tower to volume of liquid entering tower,
$x \equiv$ Distance in the tower, measured down from the top, feet,
$\phi \equiv$ A variable multiplier of the transfer-coefficient,
$f_c \equiv$ Critical flow-ratio,
$\eta_t \equiv$ Viscosity of the liquid at temp. t,
$\mathrm{V}_G \equiv$ Average gas-volume in tower,
$\mathrm{V}_L \equiv$ Average liquid-volume in tower,
$\eta_{av.} \equiv$ Average viscosity of liquid in tower,
$H \equiv$ Heat of solution of gaseous solute, calories per gram,
$z \equiv$ Fraction of height, measured downward from top of tower,
$k' \equiv$ Henry constant for conditions at top of tower,
$k'' \equiv$ Henry constant for conditions at base of tower,
$W_G' \equiv$ Weight of gas entering tower, grams per minute,
$s_G' \equiv$ Specific heat of gas entering tower,
$W_G'' \equiv$ Weight of gas leaving tower, grams per minute,
$s_G'' \equiv$ Specific heat of gas leaving tower,
$W_L'' \equiv$ Weight of liquid leaving tower, grams per minute,
$s_L'' \equiv$ Specific heat of liquid leaving tower,
$a_2 \equiv$ Density of saturated solvent-vapor at temperature T_2, grams per liter,
$a_1 \equiv$ Density of saturated solvent-vapor at temperature T_1, grams per liter,
$F \equiv$ Relative "humidity" of entering gas as regards solvent-vapor.
$L \equiv$ Heat of vaporization of the solvent, calories per gram,
$\sigma_1 \equiv$ Density of incoming liquid, grams per cc.,
$\sigma_2 \equiv$ Density of outgoing liquid, grams per cc.,
$A.C. \equiv$ Absorption coefficient, pounds solute absorbed per minute per square foot of contact-surface,
$A.F. \equiv$ Absorption factor, pounds solute absorbed per minute per cubic foot of gross tower-volume,
$r \equiv$ Per cent removal of solute from the gas,
$\psi \equiv$ Per cent saturation of the outgoing solution.

Appendix

Average Gas-Volume.—To a sufficiently good approximation, the gas-volume may be assumed to vary in the tower according to an

exponential formula analogous to that for m (Equation (20)), the volume of inert gas under outlet-conditions marking its asymptotic lower limit. The resulting average volume may be formulated in the familiar "logarithmic mean"-type formula, which simplifies to the following form:

$$\mathbf{V}_G = V_G' \left(\frac{1 - \Delta}{\log_e \frac{d_2 - d_1 + M_1}{\Delta M_2}} + \frac{d_1 - M_1}{d_2} \right). \qquad (36)$$

Average Liquid-Volume.—Use the arithmetic mean of V_L' and V_L'' (Equation (28)).

Average Liquid-Viscosity.—Use the arithmetic mean of the viscosity at temperatures t_1 and t_2.

RESEARCH DEPARTMENT,
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PRESIDENT HOWARD: This paper is open for discussion.

MR. RICHTER: I want to add one thing to this paper. Some time ago we were faced with the installation of a new absorbing system in one of our largest places, and it was judged from old-time experience that an 8-foot diameter tower, 30 or 40 feet high, would serve the purpose. A little calculation based on experience proved conclusively that we could do much better with the same height of tower, keeping the diameter down to 7 feet, showing that the increased gas flow increased our absorption in substantial proportion. I bring this out to show that without sufficient thought we may feel inclined to double up on the dimensions and conclude that if a 6-foot tower would do, we might advantageously put in an 8-foot tower, whereas more effective result may be obtained if the smaller diameter were chosen.

PRESIDENT HOWARD: Is there any further discussion? Mr. Zeisberg, can't you say something about this?

MR. ZEISBERG: This is naturally a subject in which we have been interested for a long time, but the absence of the mathematical formulas, which Mr. Van Arsdel so carefully excluded in presenting his summary of the paper, makes it impossible to give any discussion. The discussion would hinge upon these formulas.

PRESIDENT HOWARD: Any further discussion?

MR. VAN ARSDEL: Mr. President, of course the formulas will be given in the paper. I sent a copy of the paper to Mr. Haslam before

coming to the meeting, but I am not sure whether he has any comments.

MR. HASLAM: I suggest that the discussion of both papers, this paper by Mr. Van Arsdel and the paper which I shall present, be taken up at one time, because they overlap to a certain extent. Mr. Van Arsdel was very courteous in sending on a copy of his paper. I don't know that I can really discuss it without having Mr. Van Arsdel's figures in front of me, but there are several points which I will bring out in taking up the work that we are doing, and really there is not much basic difference. There is a difference in the point of view, but I don't think that fundamentally we are far apart.

THE RESISTANCE OF PACKING TO FLUID FLOW

By F. C. BLAKE

Read at the Richmond Meeting, December 7, 1922

There are very little data in the literature regarding the resistance to fluid flow of tower packings. Zeisberg[1] has reported the results obtained with air at about 15° C. for a variety of tower packings. The range of velocities used in these experiments was rather limited and it was assumed that the resistance varied as the square of the velocity. So far as the writer is aware, no attempt has been made to treat the resistance of packing materials by the method which has been used for the flow of fluids in pipes and which is commonly used in problems of aeroplane and ship design.

If P = pressure gradient, drop in pressure per unit height of packing

D = diameter of packing,
v = velocity of the fluid,
d = density of the fluid,
u = viscosity of the fluid,
M = mass velocity,

for a series of packings which are geometrically similar, the principles of dimensional homogeneity[2] lead to the equation

$$\frac{PD}{v^2 d} = f\left(\frac{vDd}{u}\right) \tag{1}$$

or its equivalent, since $M = vd$,

$$\frac{PDd}{M^2} = F\left(\frac{MD}{u}\right). \tag{2}$$

The following units have been used in applying these and subsequent equations:

M—mass velocity, thousands of lbs. per sq.ft. per hr. based on the gross cross-sectional area of the container.

[1] *Trans. Amer. Inst. Chem. Eng., 12,* 231 (1919).
[2] Buckingham, *Trans. Am. Soc. M. E.* (1915).

P—pressure gradient through the packing, inches of water per foot of height.
d—average density of fluid flowing, lbs. per cu.ft.
u—viscosity of fluid flowing, centipoises = c.g.s. units × 100.
S—sq.ft. surface of packing per cu.ft. packed space.
D—average diameter of packing, inches.
f—fractional free space in packing, thus, 0.72.

In testing the validity of this theory, the simple case of a given packing material with different fluids may be considered first. Equation (2) then becomes

$$\frac{Pd}{M^2} = F\left(\frac{M}{u}\right), \qquad (3)$$

since D, being a constant for a given packing, may be suppressed.

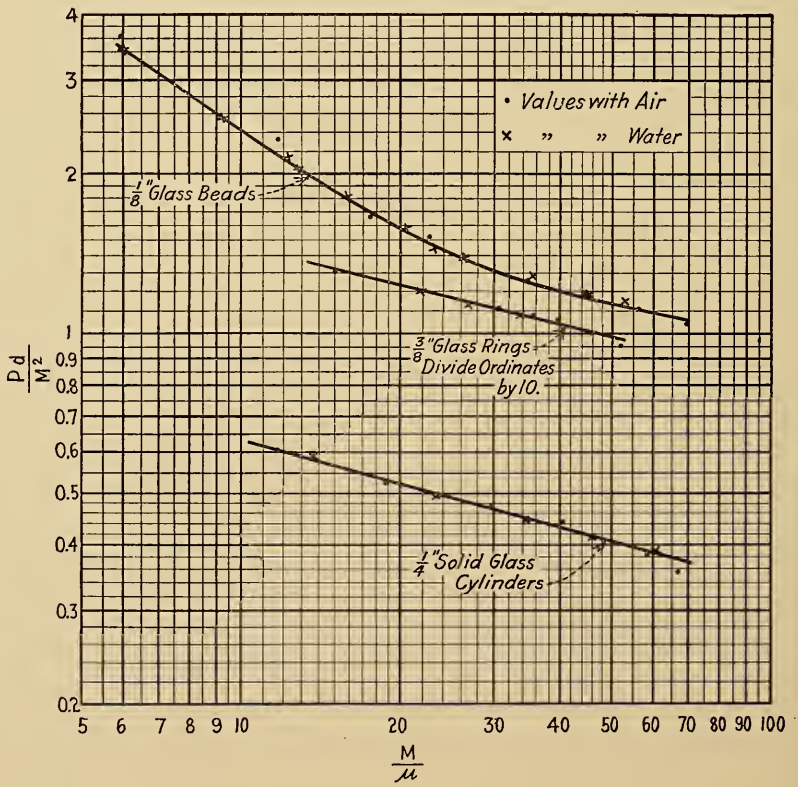

FIG. 1.

Fig. 1 shows the results obtained with three kinds of glass packings using air at atmospheric pressure and water as the fluids. Experiments made on a given packing with air at pressure of 125 mm. absolute and with carbon dioxide have given results falling on the same curve when using this method. The validity of equation (3) may be considered established, subject to the limitation in the case of compressible fluids that the drop in pressure is small compared with the total absolute pressure, so that the compressibility of the fluid may be neglected. If the average density is used, this method may be used, provided the total pressure drop through the tower is less than 20 per cent of the mean absolute pressure.

The advantages of this method of expressing pressure drops are obvious. The data obtained with any fluid may be used to estimate the pressure drop with another fluid or at a widely different temperature. The writer has estimated the pressure drop which would be obtained through a given catalyst at 600° C. from experiments made at atmospheric pressure and temperature with air in a laboratory apparatus. The actual results obtained in a plant scale apparatus checked the predicted results within less than 10 per cent.

Experiments were then made upon small glass rings, using both air and water as the fluids, and upon 1″ Raschig rings made of chemical ware, using water. The characteristic curves (equation (3)) for these packings are given in Fig. 2. Upon plotting these data in accordance with equation (2) it was at once evident that the diameter was not sufficient to specify the rings, since the points fell over a wide area rather than close to a single curve.

An examination of these packings showed that they were by no means geometrically similar. Table I gives the dimensions of the packings, the free space, and the apparent density of the packed space obtained by actual measurements. The other data are computed from these.

TABLE 1

Outside diameter, inches	0.269	0.233	0.394	0.484	1.00
Length, inches	0.281	0.219	0.375	0.449	1.03
Wall thickness, inches	0.032	0.032	0.032	0.030	0.14
Apparent density of packed space	0.70	0.829	0.498	0.393	
Percent free space	72	67	80	84.5	72
Sq. ft. surface per cu. ft. packed space	288	283	165	131	54.4
Rings in 1 cu. ft. packed space	73,000	129,000	25,700	13,700	1,240

Since the free space varied with the different packings, which would not be the case if they were geometrically similar, it was

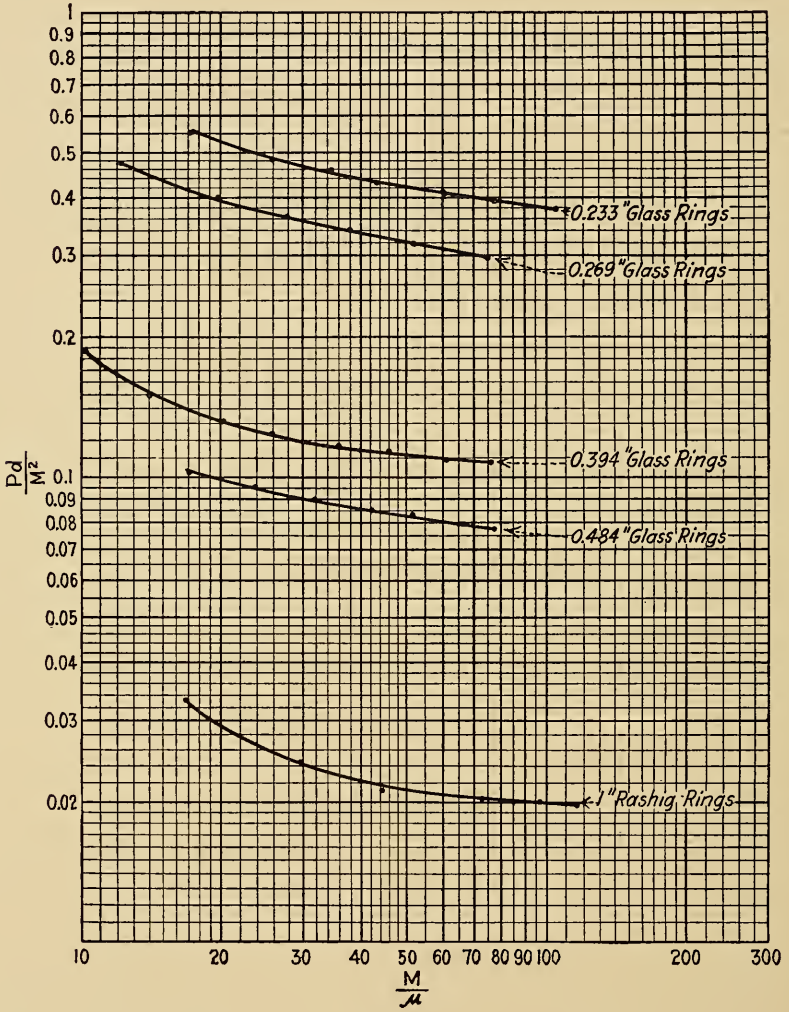

FIG. 2.

thought that the average velocity through the packing, rather than the apparent velocity based on the gross cross-sectional area of the container, would be more significant. Since the latter term is useful

in design, this effect is obtained by substituting M/f for M in equation (2). Instead of using the diameter to describe the packing, the reciprocal of the square feet of packed surface per cu.ft. of free space was used. This is equivalent to substituting f/S for D in equation (2). The equation for rings then becomes

$$\frac{Pf^3d}{M^2S} = F\left(\frac{M}{Su}\right). \tag{4}$$

Fig. 3 gives the data for rings plotted in accordance with equation (4). The data for the glass rings now fall along a curve which may be approximated by the equation

$$\frac{Pf^3d}{M^2S} = 0.0003\left(\frac{M}{Su}\right)^{-0.2}$$

$$\text{or } P = 0.0003\frac{M^{1.8}S^{1.2}u^{0.2}}{df^3}. \tag{5}$$

The Raschig rings give distinctly lower results than the glass rings in Fig. 3. The pressure drop obtained with the Raschig rings is less than that reported by Zeisberg, but another set of measurements gave essentially the results obtained before. The discrepancy between the

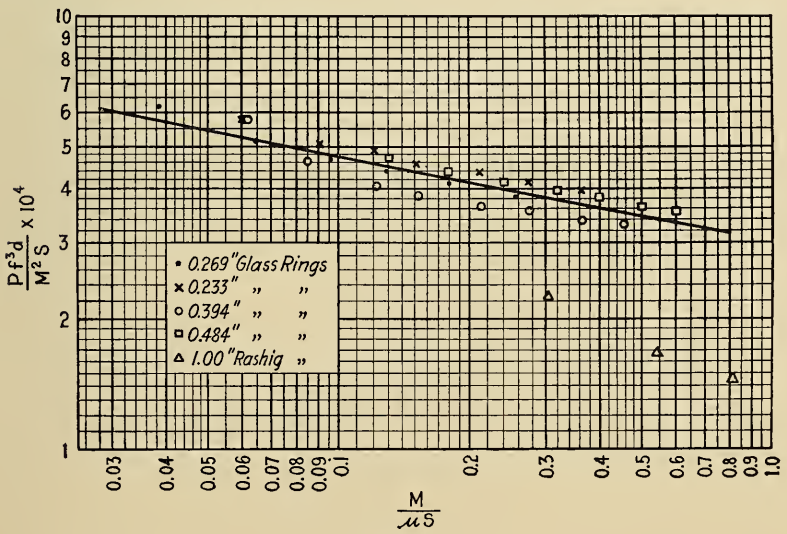

FIG. 3.

results obtained with glass rings and Raschig rings is still unexplained. It was thought that, in the case of the small rings, the flow of fluid through the interior of those rings whose axes were nearly horizontal might be so small that the effective free space was less than the total free space. Some rings were put in a vertical glass tube filled with strong permanganate solution and water allowed to flow in at the top, displacing the permanganate. While there was some diffusion between the water and the permanganate, the dividing line was fairly well defined and traveled down the tube at a rate equal to that of the water addition without leaving any rings whose interior was colored by permanganate.

In an attempt to secure a series of packings which would be more nearly geometrically similar than the rings used, broken pumice was graded into several sizes by screens and the data obtained on the various sizes plotted in accordance with equation (2). Fig. 4 shows the result. The variation from geometrical similarity of the different particles was sufficient to make equation (2) only an approximation in this case, but nevertheless useful for estimating purposes.

Some possible sources of trouble in using this method of esti-

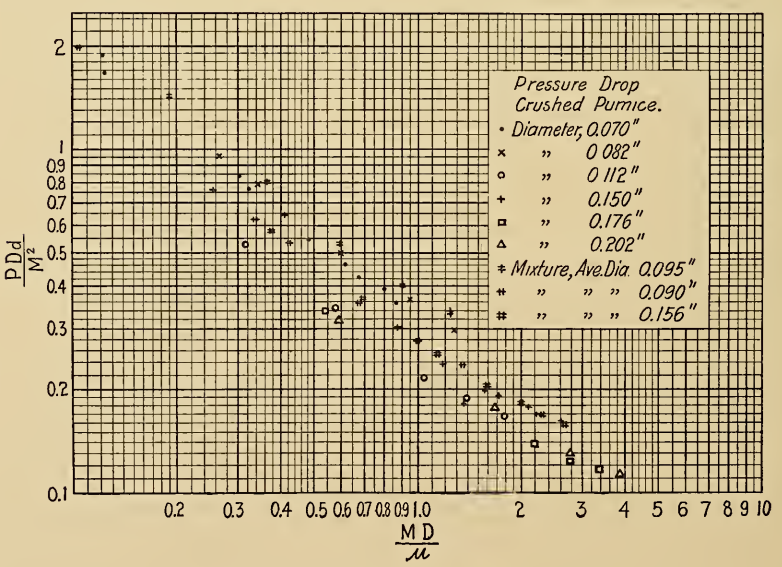

FIG. 4.

mating pressure drop may be pointed out. The restrictions in the case of compressible fluids have already been stated. It may be mentioned that the viscosity of a gas is a function of the temperature alone and is independent of the pressure. There is also no satisfactory method of predicting the viscosity of a gas mixture from the viscosity of its components.

In the case of rings, a decided resistance may be introduced by the support, unless care is taken in packing the lower layers. When rings are dumped on to a screen the lower layer tends to arrange itself with the axes of the rings parallel to the screen, thereby forming a decided constriction at that point. In the case of granular packings, if the diameter of the holes in the screen or grid is only slightly smaller than the diameter of the packing, the grid is liable to become badly plugged and a high resistance introduced. In the data presented in this paper any resistance introduced by the support has been eliminated.

With granular packings such as pumice, where the size is not uniform, it has been found that the effective diameter to be used in equation (2) may be computed from the screen analysis by the equation

$$\text{Effective dia.} = \frac{\Sigma W}{\Sigma \frac{W}{D}},$$

where $\Sigma \frac{W}{D}$ = sum of terms of form $\frac{\text{wt. of material of diam. } D}{D}$,

ΣW = total weight of material.

This is equivalent to assuming that the effective diameter is that diameter which with material of uniform size would give the same surface per cu.ft. of packed space as the graded material.

Experimental Station,
E. I. du Pont de Nemours & Co.

USE OF PROPANE FOR REFRIGERATION

By H. D. EDWARDS

New York, N. Y.

Read at the Richmond Meeting, December 7, 1922

The thought of using the hydrocarbon gases as refrigerants dates back at least to 1867, when patents were issued covering the manufacture and application of hydride of propyle or chimogene and hydride of ethyl, "to the making of ice and cooling in general."

Rapid strides in the art of separation of gaseous mixtures into their constituents have made possible a high purity commercial production of all the members of the paraffin series, especially those having the lower boiling points, namely, methane, ethane, propane, and butane. The last three of those mentioned have definite allocations in the refrigeration field.

Butane has a boiling point of about 1° C., and thus for some time at least will probably be confined to use in the small refrigeration unit where low temperatures are not required.

Ethane with its low boiling point of a minus 93° C. is especially adapted to use in refrigeration cycles where extremely low temperatures are desired. At present ethane is used in the standard carbon dioxide system; however, the usual condensing pressure is about 400 lb. less and the temperature obtainable is about 20° C. lower than can be reached with carbon dioxide.

Propane boils at minus 44.5° C., as compared with a boiling point of a minus 33.5° C. for ammonia. It condenses to a colorless liquid having a specific gravity of 0.536 at 0° C. and atmospheric pressure; the density of the gas under like conditions is 1.56 (Air = 1). Its critical temperature is 97.5° C., and its critical pressure 45 atmospheres. It remains a liquid at — 195° C.

The demand for information on the properties of propane when used as a refrigerant has been so insistent that a table of such properties has been prepared by Mr. H. E. Thompson, assisted by Mr. G. K. Bohn, and with his permission I am presenting this table for the first time. As such a table can not be presented by reading, copies are available for those interested.

The sources of information on which this table is based are given in Chart No. 1—showing the vapor tension; Chart No. 2—giving the volume per lb. of both liquid and vapor and their corresponding densities; Chart No. 3—giving the values of dp/dT and $v''-v'$; and the resulting Chart No. 4—giving the latent heat. These tables are all constructed on the Fahrenheit basis, as this unit is used almost exclusively in the usual refrigeration work.

Mr. Thompson comments as follows on these charts:

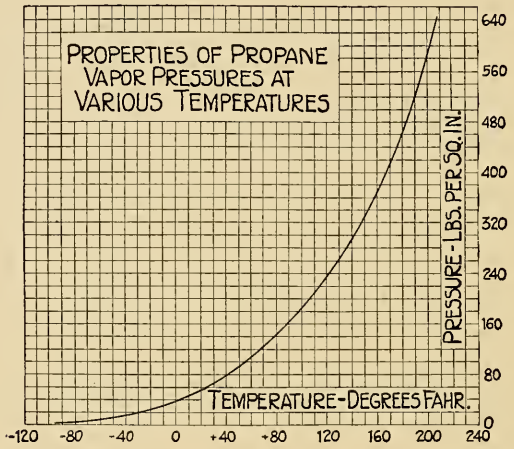

CHART I.

"The vapor pressure curve used takes the values of the Bureau of Mines for pressures below one atmosphere, the values from Landolt and Börnstein for intermediate points, and for the higher pressures the data of Hainlen as given by the Metric Metal Works."

"The data for density have been obtained from several sources and from our experimental work. The liquid values at low temperatures are from the *Journal of American Chemical Society,* those at high temperatures from our experimental data. The vapor densities at low temperatures are from the gas laws used in conjunction with the present accepted value of the density of propane. The intermediate values use the Bureau of Mines data on compressibility, and the values at temperatures above 80° F. are from Van der Waals' equation. These data are com-

bined in the lower curve, which shows the 'dome' for propane and the 'mean density' curve."

"The values for the slope of the vapor pressure curve (dp/dT) were derived by the graphical method and plotted.

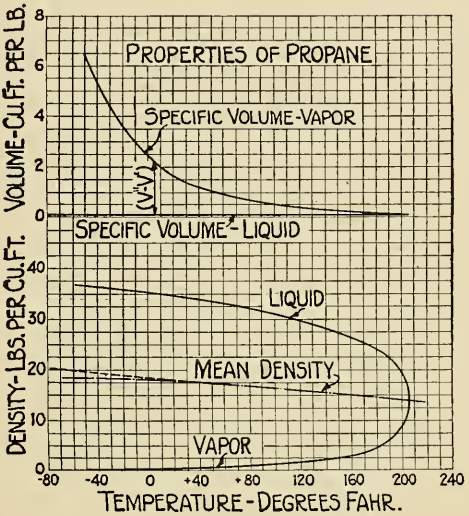

Chart II.

The values for the difference in specific volume of the vapor and liquid are also plotted. The actual work of arriving at the values shown was carried out on curves drawn to a much larger scale.

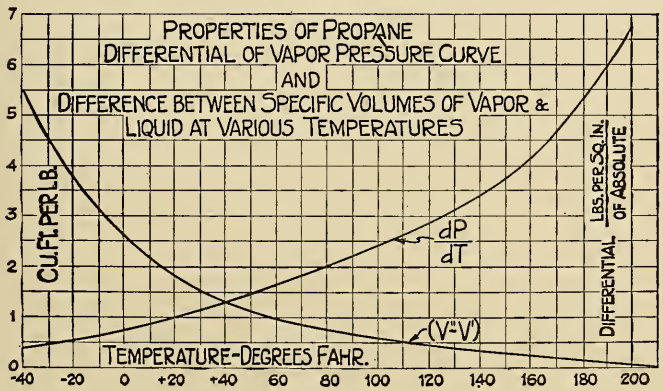

Chart III.

The accompanying blueprints are merely for the purpose of showing the method and the trend of the values. The numerical values for (dp/dT) and $(v''-v')$ are recorded in the 'Table of Properties' along with the other data."

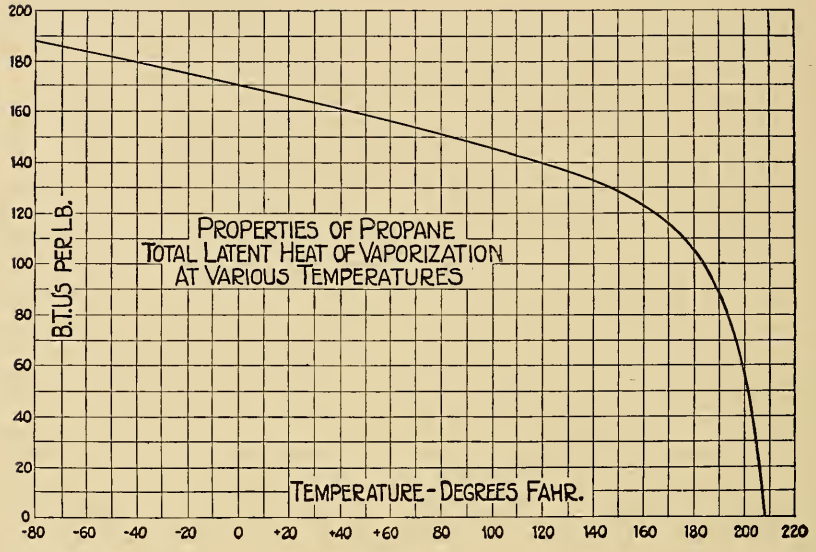

CHART IV.

"The values of latent heat of evaporation were computed from these data by the Clapeyron-Clausius equation:

$$\text{Latent Heat } r = AT\ (V''-V')\ \frac{dp}{dT},$$

in which A is the reciprocal of the mechanical equivalent of heat."

The specific heats of both the liquid and gas must be determined before the exact net refrigeration effect of evaporating propane can be calculated. These values will be published within the next few months.

Propane has a particular field of application outside of the usual lines of ice making, cold storage, etc., on account of the lower temperatures that may be obtained with it when used in a refrigeration cycle. Comparing propane with ammonia, we find that 1-lb. positive pressure on the suction side of the compressor corresponds to an

evaporating temperature of a minus 44° F. for the former and a minus 25° F. for the latter. Even with this lower temperature the ratio of compression is less for propane than for ammonia, as is shown by Chart No. V, which gives the vapor tension for these two gases.

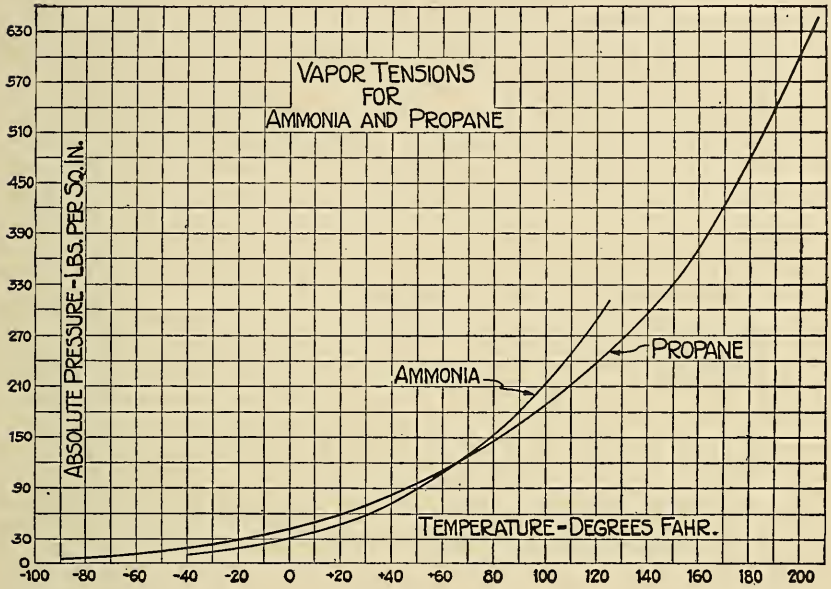

CHART V.

This chart shows that at the usual condensing temperatures the pressure of propane is from 10 to 20 lb. less than that of ammonia.

From construction and operation standpoints propane has very desirable characteristics, outside of possible capacity and power advantages, which depend on many conditions, namely:

1. It has no corrosive action on any metals.
2. It forms no injurious acids with water.
3. It is perfectly stable under any conditions required in refrigeration work.
4. It can be used in a standard ammonia unit with excellent results.
5. Lower temperatures are obtainable than with ammonia.
6. Its presence is not dangerous to health until its density is sufficient to exclude the oxygen necessary during respiration.

7. Practice has already proven that the hydrocarbon gases are the best for use in household and small units where operation for long periods without attention is essential.

Propane is inflammable and open flames should not be permitted where its vapors may collect. In small units special attention must be given to the lubrication problem as with other refrigerants. A suitable lubricant has been developed for these machines. The usual lubrication employed in both inclosed vertical and horizontal ammonia compressors has been found entirely satisfactory when propane is used. There is less mulsification with propane than with ammonia.

Propane has assumed a definite place in refrigeration practice and its characteristics are such that its use should become general as these characteristics become known and are appreciated.

December, 1922.

Discussion

Dr. F. W. Frerichs: I should like to ask Mr. Edwards whether he made any experiments with mixtures of propane and ammonia used together in the same refrigerating machine? I have learned from circulars that such mixtures can be used and are beneficial.

Mr. Edwards: The information given in the circular was based upon practical operating experience. However, we have not determined definitely whether these can be mixed in all percentages, and I doubt whether they can be. It seems hardly probable, although some claim to have done it.

Dr. Frerichs: I understand that propane is made from casing head gas, and that butane, propane, and ethane are separated by distillation. Is there any security that the separation of these substances is really perfect? I ask this question in view of the statement that if not enough propane could be made a mixture of butane and ethane could be substituted.

Mr. Edwards: One of the great problems in connection with the production of these gases was the working out of a suitable method of rapid analysis. In regard to the purity of these gases, they are all over 99 per cent pure. The only impurities in propane are slight traces of ethane and butane. They are obtained from natural gas and are separated by liquification and rectification.

Dr. John C. Olsen: How does the cost compare with the cost of ammonia?

MR. EDWARDS: At the present time propane is not on a competing basis with ammonia in regard to price.

DR. OLSEN: Can you ship it in cylinders, just as you ship ammonia?

MR. EDWARDS: Yes; it is shipped in cylinders in various quantities. Special cylinders have been made for it somewhat similar to ammonia cylinders. Propane cylinders, however, have the usual fusible plug, safety devices, etc.

PRESIDENT HOWARD: Is it shipped in liquid condition?

MR. EDWARDS: Yes; in a liquid condition.

MR. JOHN M. WEISS: Is the use of propane likely to conflict with local fire regulations, and are special precautions necessary around the refrigerating plant? Do they permit its use in a large city for large refrigerating plants such as in a hotel?

MR. EDWARDS: That has not been determined. The use of propane is in its infancy, and what rules and regulations will be necessary for safety can only be determined in time.

DR. OLSEN: Do you anticipate that propane will replace ammonia?

MR. EDWARDS: I think not.

DR. OLSEN: It will have its own special field of application?

MR. EDWARDS: I think so.

DR. FRERICHS: Do you think the sources of supply, exclusively from gas wells, will be sufficient to supply the American market?

MR. EDWARDS: At the present time it is almost inexhaustible. Some natural gas wells have more propane than others.

MR. CROSBY FIELD: In view of the frequently experienced requirements of low temperatures in some operations, the advent of propane has been looked forward to by us with great eagerness, but we should like some definite information as to the safety from fire and also some way of getting around the flammability. Its mixture with a small percentage of an odorizer, like ammonia, seems to be an ideal way. If you could work that out so that we could tell leaks by the smell of ammonia, it would be of some advantage.

MR. EDWARDS: Several things are being tried out as odorizers. Amyl acetate leaves a very "nice" smell, and a few things like that have been tried. The problem is to put in something that will be permanent, which will retain its odorizing properties when the refrigerant goes through the usual cycles of condensation and evaporation.

Dr. Frerichs: In regard to the inflammability of mixtures of propane and ammonia, ammonia is not explosive and inflammable unless it is mixed in very definite proportions with air. The mixture of 18 per cent ammonia gas and 82 per cent air will explode or burn. A mixture of 26 per cent ammonia and 74 per cent of air will also burn. A mixture containing between 18 and 26 per cent of ammonia will burn, but outside those proportions it will not burn. A small percentage of any hydrocarbon, about 1 or 2 per cent, contained in ammonia will make ammonia itself inflammable, and a mixture of 2 per cent hydrocarbon and 98 per cent liquid ammonia will burn like any hydrocarbon.

Mr. Huff: I should like to suggest to the writer of the paper that a valuable addition would be information on the explosive limits of propane.

Mr. Edwards: They were determined by Thomsen in 1886 and these values have been quoted since. In the last two or three weeks we had occasion to repeat those tests and found the explosive limits of propane were 2.4 to 7.4. We also determined the explosive limits of ammonia and found that the explosive limits were from 13.0 to 26.8, a little wider range than has previously been given.

These experiments were carried out under exactly the same conditions. The force of the explosion was also measured by impact against the mercury column and it was found, in general, that the impact of explosion of ammonia was more than the impact of explosion of propane. We had not expected such results.

At the same time we carried on experiments with methyl chloride and ethyl chloride under the same conditions. I do not remember the results, but they have a very much wider explosive range than was previously supposed.

Mr. Crosby Field: Did you try any admixtures of small percentages of lubricating oil?

Mr. Edwards: No; we intend to conduct experiments with the different lubricating oils, with iron oxide, and other things which might be present in the refrigerating machine.

Dr. Parsons: I want to suggest the use of chloracetophenone, which is a special tear gas. More recently it has been used on ships to mix with the poison gas used to kill vermin.

Mr. Edwards: We have not tried that. We have tried the substances which have been recommended by the Bureau of Mines for

mine work, such as butyl-mercaptan and ethyl-mercaptan. Not being a chemist, I can not discuss their chemical properties.

DR. PARSONS: This will be far more effective than any of those mercaptans.

MR. EDWARDS: I appreciate the suggestion very much.

DR. HUGH K. MOORE: As this paper will probably be printed, I dislike to see anything go into the *Transactions* which might be wrong, and I should like to ask Mr. Edwards if there is not an error here in the boiling point of ethane, stated in your fourth paragraph [referring to preprint of Mr. Edwards' paper]. I do not say this to criticize, but to prevent you from having criticism later.

MR. EDWARDS: I thought that was approximately correct. I don't know that we have actually determined it.

DR. MOORE: In 1909 we determined that very carefully, and it was 92.5°.

MR. EDWARDS: 92.5°?

DR. MOORE: Yes; 92.5°. You also sent us several cylinders recently, and we got a temperature of minus 135° Fahrenheit on all of it, which checks also very closely, within about 0.2°, with the temperatures which we had previously determined. So I was wondering if there was not a possible error here. Also, the literature on the subject I am very sure shows it ranging all the way from 91° to 93° Centigrade.

MR. EDWARDS: I believe that the boiling point given is taken from the Smithsonian Tables, and I believe that we did not determine the boiling point ourselves.

DR. MOORE: I am very much interested to have Mr. Edwards present this paper here, because we are interested in work with a small plant. I am not interested in propane, but in refrigeration with ethane which gives a lower temperature, necessary for the work that we are doing, and we expect shortly to put up a plant using ethane.

In 1909, when I started, we could not buy ethane, and we had to make it. And we obtained a very pure product from ethylene in this way. I wish to add, also, that these saturated hydrocarbons have properties that no other hydrocarbons have. In the first place, you can not use ethylene, for the critical temperature is too low in the summertime and you have to resort to double refrigeration, which is too expensive. You can not use acetylene gas, for it explodes too

readily. If you have a saturated hydrocarbon, it does not seem to break down in any way in handling, and it has special advantages in relation to the low specific heat of the liquid, so that you do not lose so much in cooling the liquid. This relation between the specific heat of liquid and that of the gas gives you very valuable properties.

When you pack a compressor cylinder at low temperatures, you freeze almost anything that you put in to lubricate your cylinder, whereas if you have the cold gas coming back, say, at minus 135° Fahrenheit, through an exchanger cooling the liquid and heating the gas, you can keep within the temperatures of lubrication usable in the stuffing box.

We have been conducting experiments with ethane, especially in the liquification of chlorine. I had liquid chlorine at that temperature taken right into Mr. Brown's [the President] office, without saying anything. When chlorine gets down to —100°, they could not smell it if you said nothing about it. But they would smell it anyway if you said anything about it. Ethane provides one of the simplest methods of putting chlorine into a condition at that temperature where there is no odor or anything else. You avoid all the pumping difficulties of chlorine, and it is of a great deal of importance; and because of its similarity to ethane, I wanted Mr. Edwards to give a paper about plants running on propane.

Note.—Mr. Edwards later verified the boiling point of ethane as 93° C., that given by Mr. Moore.

Dr. Frerichs: Very low temperatures are now obtained in the Syracuse plant of the Solvay Company, where they are using the Haber process. They have to cool, in order to separate ammonia from the other gases, and I am not quite sure but that the temperature is below zero Fahrenheit, which they obtain by ammonia machines. They only use machines with a two-stage compressor, and have a back pressure of about one pound only. In the first stage they compress to 15 pounds, and then in the second stage they finish the compression and liquification of the ammonia. Such a machine is operating in the Syracuse plant of the Nitrogen Company there.

Dr. Moore: We are talking about minus 115° and minus 120° Fahrenheit.

Dr. Frerichs: That would be equivalent to temperatures reached with carbonic acid machines.

Dr. Moore: You can not do it with carbon dioxide. It freezes

solid at minus 56° Centigrade. The Kroeschell people said they could do that and we undertook to do it, and the first thing I knew I plugged every expansion pipe at minus 56° Centigrade. Part of it will give a 20-lb. pressure per square inch and the other will be solid, and will fill up the condenser right solid. These hydrocarbons solve the difficulty and give a positive pressure on the condenser, so that air will not be sucked in through the stuffing boxes. As to odor, I think it has sufficient odor, so that I don't think it has any need of having something else mixed with it. It smells like gasoline. What you must have is something that is not endothermic, that will not explode, and you can use this in a CO_2 machine, by only putting on a larger low-pressure cylinder. With the back pressure on a CO_2 machine, you get a tremendous amount of gas into the cylinder. But if you use a 25-ton machine under these conditions, you would get very much less refrigeration at 5 or 10 pounds back pressure, and the efficiency of the machine is very low. Therefore you have to put in a low-pressure machine to bring it up to the original pressure of the CO_2 machine in order to get the capacity.

Another difficulty is that for the same temperatures the pressures of liquification are much less with ethane—very much less. In fact, several hundred pounds less than with CO_2.

PRESIDENT HOWARD: I think this is very interesting, but time is getting on, and we will have to call the discussion closed and pass to the next paper.

THE MEASUREMENT OF STIRRER PERFORMANCE

By J. C. WOOD, E. R. WHITTEMORE and W. L. BADGER

Read at the Richmond Meeting, December 8, 1922

A Method of Measuring Stirrer Performance is Suggested and Experiments in Which It Has Been Applied to the Ordinary Paddle Stirrer are Described—the Surprising Efficiency of a Paddle Stirrer Also is Discussed

The purposes for which stirrers are used may be analyzed as follows:

1. To mix two or more mutually soluble fluids.
2. To emulsify two or more mutually insoluble fluids.
3. To hold an insoluble solid in suspension in a fluid.
4. To dissolve a soluble solid.
5. To mix two or more viscous, pasty, or solid materials.

Evidently the performance of any given device will be different when applied to the various uses above enumerated; and in many cases in practice a given device will be of appreciable value only in one of the cases. Case 4 is perhaps only a special case of case 1, since it consists mainly of removing a film of saturated solution from the surface of the crystals and mixing it with the bulk of the solvent. It is hoped to present a paper soon on this phase of stirring.

The theory of stirring has never been discussed to the writers' knowledge; nor are there in the literature any quantitative data on the performance of any type of stirrer, from either the standpoint of power consumption or time for complete mixing. The writers have no mathematical theory to offer. We believe, however, that the fact that our experimental data seem to be unique gives them importance in spite of the fact that they are purely empirical.

Experimental Methods and Equipment

The tank used in this work was a wood tank about 5 ft. in diameter by 5 ft. high, and held about 600 gal. It was provided with a

paddle stirrer (shown in Fig. 1). It had a vertical wood post (3 x 3 in.) standing in a simple step bearing and rotated by bevel gears and a countershaft. To this vertical post was attached a blade formed of a 3 x 3-in. timber shaved off at an angle of 45 deg. as indicated. This type of stirrer is very common and is regularly furnished by practically all makers of tanks.

The principal problem was, obviously, to determine when the tank was stirred. Sampling tubes of seamless copper ¼ in. inside diameter were inserted at four levels (1, 2, 3, and 4 ft. from the bottom of the tank) and extended in for three different radial distances at each level. Fig. 1 is a view of the inside of the tank showing these tubes. These proved to be stiff enough to hold their position with the most violent stirring used. They were brought down the outside of the tank and all ended at a common level, so that the hydrostatic head on the outlet was the same for all.

At first, methyl violet was used. It was added in the form of a paste in water. Samples were taken from all tubes every 30 seconds and measured in a colorimeter. This was very slow and very trying

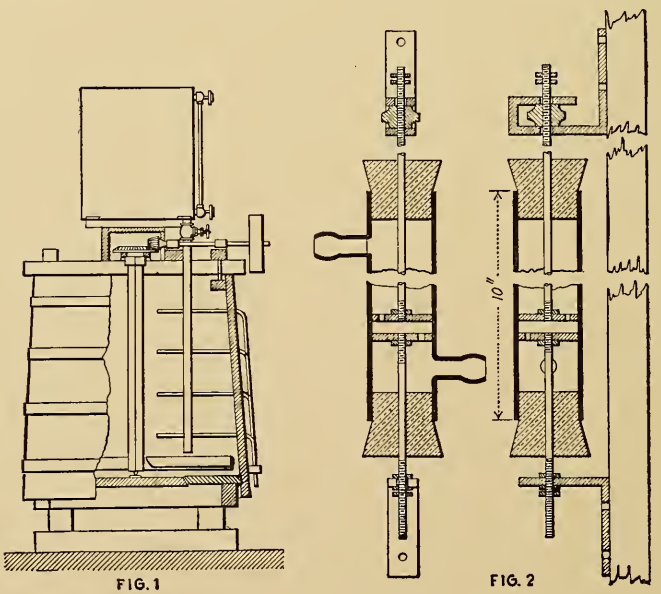

FIG. 1. Arrangement of Apparatus
FIG. 2. Details of Conductivity Cell

on the eyes, and the work was greatly delayed by cloudy days. Also occasional tarry lumps of the dye would lodge in the end of one of the sampling tubes and spoil the whole run. This method was therefore abandoned.

Next was tried the addition of strong commercial hydrochloric acid with titration of the samples. This was also very slow and tedious. It took 4 to 5 hours to make a test and analyze the samples. This preliminary work, however, showed that stirring was quite rapid. Most of the runs indicated a time of stirring of about 1 minute.

The Conductivity Method Finally Adopted

Finally the two junior authors developed a method based on electrical conductivity which promises to have a wide range of usefulness. A number of crude conductivity cells were made, and mounted so that liquid from the sampling tubes could be drawn through them. Several different types were used, but the form shown in Fig. 2 was found to be the most useful. The electrodes were of brass, but with alternating current no troubles were experienced from electrolysis. The position of the upper electrode could be accurately adjusted. In the tests here reported, four or five such cells were connected in series electrically, with a total drop of 220 volts across the set. Through each one was drawn a stream of liquid from one of the sampling tubes, and across each one was connected a voltmeter. The electrodes were adjusted before a test so that all the cells had the same electrical resistance at the start.

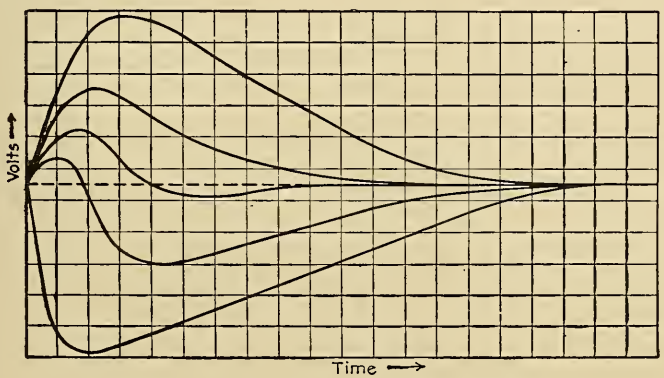

Fig. 3. Theoretical Voltage Changes

The tank was first filled with city water and then a small amount of saturated sodium chloride solution was run in from a storage tank. The amount used corresponded to 4 lb. solid salt per foot of water in the tank. The arrangement (shown in Fig. 1) permitted this solution to be added at the bottom of the tank. The stirrer was then started and readings taken of voltage changes, current, speed, and power consumed. The routine was developed to the point where a run with all its data could be made, the tank dumped, and made ready for the next run in 10 minutes. A preliminary study showed that the points nearest the center at each level were the last to come to equilibrium with the rest of the tank. Through a large part of this work only four voltmeters were available, and hence the sampling tube at the inner point at each level was used.

Adding strong salt solution to the bottom of the tank should decrease the resistance of the bottom cell, and hence decrease the voltage drop across it, while increasing the voltage drop across the other cells. As the salt is mixed with the tank contents this resistance should gradually rise to its final value at equilibrium. In the same way, the voltage across the second cell from the bottom should first rise, because, though its resistance had not changed, the decreased voltage drop across the bottom cell should increase the drop across all the others. But when the level of the salt solution rises to the second sampling tube, the resistance of the second cell (and its voltage also) should suddenly drop, with a corresponding increase in the voltage of the cells above it.

Discussion of Results

Theoretical Value of Conductivity

Based on such a line of reasoning, the change in voltage drop across the cells should be as shown in Fig. 3. Actual data from a typical run are shown in Figs. 4 and 5, exactly confirming the theory. Fig. 4 represents a run with water 4 ft. deep, and Fig. 5 one with water 3 ft. deep. In Fig. 4 cell 1 was connected to the center sampling tube 1 ft. from the bottom, cells Nos. 2, 3, and 4 being the corresponding points at the 2-, 3-, and 4-ft. levels. In Fig. 5 cells 1, 2, and 3 connect to the same tubes as before, but cell 4 was connected to the outer tube at the 3-ft. level. These runs were made with a cruder type of cell than the one shown in Fig. 2 and they could not be accurately adjusted for equal resistance (and hence equal voltage drop).

The way in which the curves of Fig. 4 correspond to our theory is most satisfactory. As strong salt solution is stirred and passes upward, the resistance of the cells suddenly decreases in regular order and the voltage across the rest rises. A most interesting point in

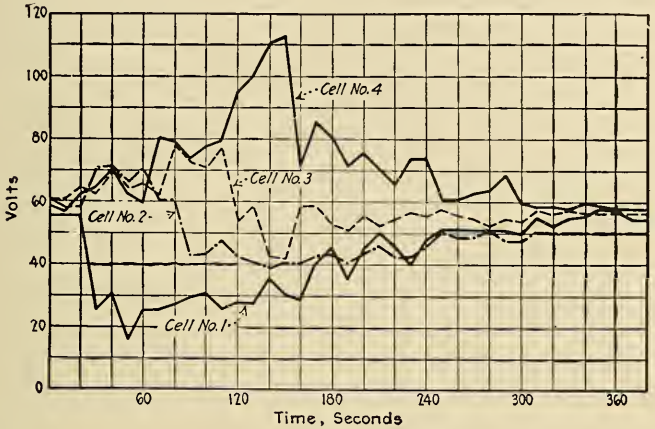

FIG. 4. Actual Voltage Changes. $7\frac{3}{4}$ R.P.M., 4 Ft. Level

Fig. 5 is that the outer *top* cell shows salt before the inner *bottom* cell. This is the result of a centrifugal component of the action of the stirrer, transformed into a vertical current of strong solution by the tank wall.

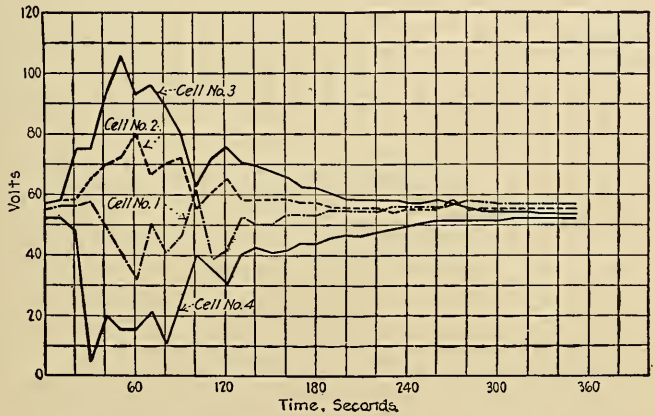

FIG. 5. Actual Voltage Changes. $7\frac{3}{4}$ R.P.M., 3 Ft. Level

Through most of the work the stirring was so rapid that changes in the voltmeter readings could not be followed. It was observed that the current in the circuit rose and became constant at about the time the voltmeters became uniform. By reading the ammeter every 10

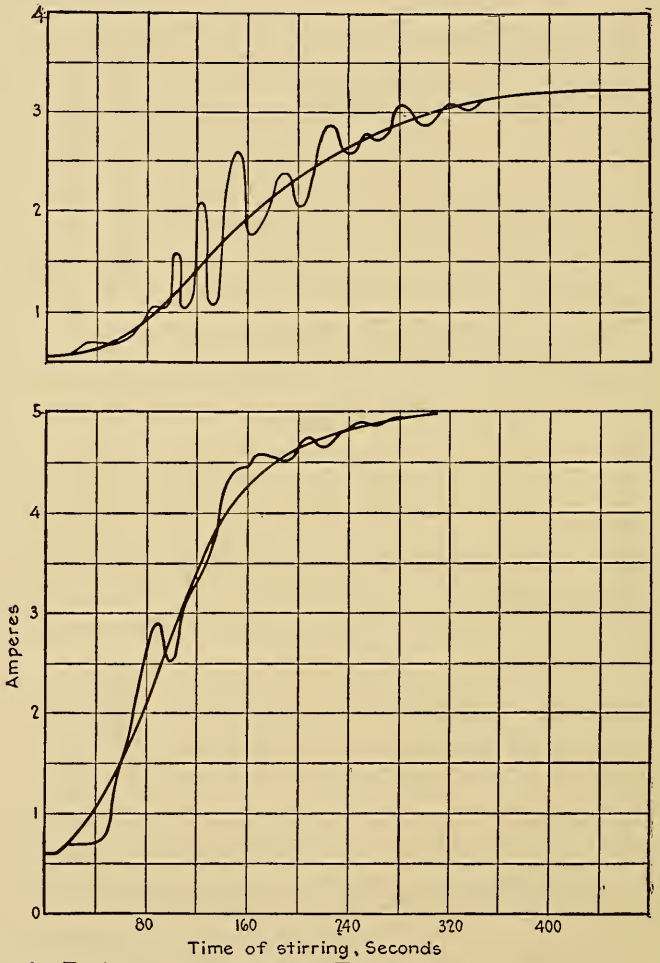

FIG. 6. Typical Current-Time Curves, 7¾ and 10 R.P.M., 4 Ft. Level

seconds a current-time curve could be plotted, which approached an asymptote parallel to the time axis as stirring became complete. Most of the work was based on this curve. Samples of such curves are shown in Fig. 6. The pulsations in the observed curve represent

slugs of strong solution swept past the ends of the sampling tubes by the rotation of the stirrer. A smooth mean curve was put in for purposes of computation. A curve which approaches an asymptote

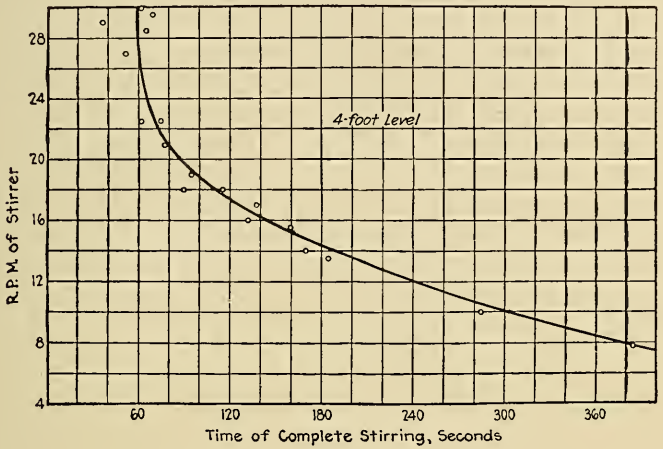

FIG. 7. Stirrer Performance

does not give a satisfactory end-point. The first derivative (determined graphically) was plotted for each of the current curves, and an arbitrary end-point taken as the time when $\frac{dc}{dt} = 0.04$ (c = current in amperes, t = time in seconds).

Vertical and Horizontal Uniformity

In the case of runs at the 4-ft. level, when time of stirring was long enough to permit following the voltmeters also, it was found that the voltmeters became constant before the current did. This means that a uniform vertical distribution existed, but that due to centrifugal action there was still a non-uniformity in a horizontal plane. The difference was great enough at very slow speeds to be unmistakable. Hence in all cases the end-point was taken from the curves for current.

From these methods of reading the curves of Figs. 7 and 8 have been plotted. The determinations of Fig. 7 were made with the tank filled with water to a depth of 4 ft., and those of Fig. 8 to a depth of 3 ft. The most striking thing about these curves is the short time

necessary to mix this tank thoroughly with what would ordinarily be considered a very inefficient stirrer. The second point is that an increase in speed for this stirrer above 18 to 20 r.p.m. is useless so

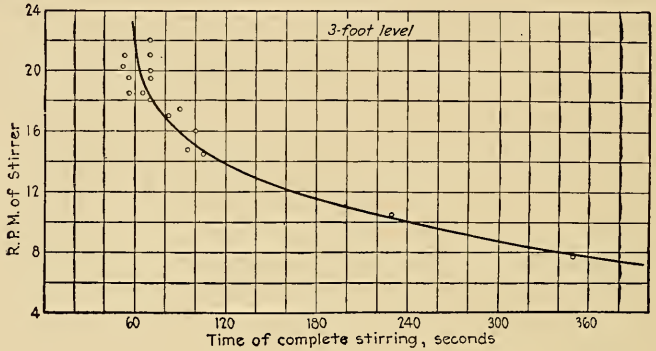

FIG. 8. Stirrer Performance

far as time of stirring is concerned. In fact, in the vicinity of 30 r.p.m. there seems to be a break in the curves, and at rates above this mixing seems actually slower than below this speed.

The Illusion of Visible Swirl

Another feature that does not appear in the experimental data, but which is interesting, is that at all speeds the contents of the tank seem to be rotating as an even, homogeneous mass. The advocate of some special type of stirrer would insist that the contents of the tank were not being stirred at all. There was no visible swirling, eddying, churning, or other indications of crossing of lines of flow. That this type of motion may produce very rapid and efficient mixing is a new thought in stirrer design. One needs but to consider the *apparent* motion of a fluid in a transparent tube at velocities above the critical. Small visible suspended particles move, apparently, in straight lines; yet the flow may be fully turbulent. Visible motion is due to particles of suspended solids which may very well have inertia enough to flow in fairly straight lines in spite of the fluid turbulence around them. So in mixing two mutually soluble liquids (as salt solution and water) the visible motion of the mass is not an index of the true degree of turbulence.

Measurements of power consumed were not satisfactory. So much power was consumed in shafting, belting, gears, etc., that the

power actually used for stirring was too low to measure for the slower speeds. Power measurements were simplified by the fact that a d.c. motor was used. Shunt field power was determined once and considered constant (as the control rheostat did not affect the voltage

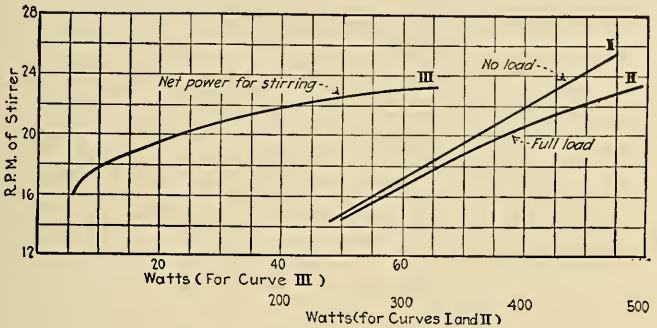

FIG. 9. Power Consumption

Curve I, no load. Curve II, full load. Curve III, net power for stirring.

across the shunt coils). Power in the armature was determined from a properly connected voltmeter and ammeter in the armature circuit. A power reading was taken at a given speed with the tank empty, and again at the same speed with the tank filled with water to the desired height. The difference was considered the net power consumed in stirring. At slow speeds it was so small as to be less than errors introduced by fluctuations in the instruments. Such data as were determined are shown in Fig. 9. Here curve I is the no-load power consumption, curve II the full-load power consumption, and curve III the net power for stirring. This indicates clearly the very small amount of power really used at any reasonable speed and the relatively rapid increase in power at higher speeds. The point where a rapid rise of power consumption occurs without a perceptible increase in time of stirring is one of the useful results to be obtained by applying this method of analysis to the stirring device.

Studies are now under way on rate of dissolving crystals and on the characteristics of propeller stirrers.

CONCLUSIONS

1. A plain paddle stirrer is a much more efficient mixer for miscible liquids than is usually supposed.

2. For the conditions of this set of experiments, a 600-gal. tank

was thoroughly stirred in less than 1 minute at any speed above 22 r.p.m., though above 30 r.p.m. there seemed to be an increase of stirring time.

3. The visual appearance of a tank of liquid being stirred is not a measure of the efficiency of the stirring apparatus.

4. At the speed above which there is no gain in time of stirring there is a rapid rise in net power consumption.

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DISCUSSION

MR. CROSBY FIELD: From the viewpoint of the men who have to approve drawings of stirrers of various kinds, I should like to say that this paper which Professor Badger has given us has put us everlastingly in debt to him. I regret, however, that Prof. Badger limited himself in the beginning of his paper to certain kinds of agitators, or to agitators for certain purposes. We believe in our work it is better to make a different kind of classification. Therefore, we classify them according to the general purpose for which the agitator is desired, and then according to the specific kind.

The main purposes of agitation may be defined as follows:

1. To control the period of contact of one reactive particle with another. Examples: The usual chemical reaction, the dissolving of solids by liquids, the washing of precipitates, etc.

2. To assist in heat transfer by increasing unit velocity of liquid or gas particles over a heat transfer medium. Examples: The common steam-heated, agitated reaction vessel.

3. To assist in the rapid diffusion of heat throughout a liquid or gaseous mass. Example: The heating of large agitated vats by a coil in the bottom.

4. To assist in the rapid diffusion of particles of a mass from one or more central feeding points. Examples: Ordinary nitrators, etc.

5. To control the size of crystals and the rate of their formation. Example: The ordinary jacketed crystallizing pan.

6. To cause a liquid to become a vehicle for solid particles or a gas to become a vehicle for liquid or solid particles. Examples: Dorr classifier and settling tanks, slurry tanks, etc. The following are the principal types of agitating machinery in general use:

(*a*) Movement of the containing body. Examples: Laboratory shaking devices, rotary cement kilns, ball mills when used without pebbles or balls. In this type the agitation or mixing function is performed by combining the motion of the containing vessel with that due to gravity.

(*b*) The chaser type of agitator. In this a body foreign to the mix is permitted to travel with more or less free motion due to combination of gravity and the motion of the containing vessel. As example, we have pebble mills with the stones left in them. It is thought that stills having chains which scrape the sides of the vessel, which chains are operated by a motion coming under the above definition, should be included here.

(*c*) The paddle agitator. This is the one most frequently met with and has numerous modifications. In its simplest state it is merely a paddle on a shaft. Either the shaft or the containing body rotates so that there is relative motion between the paddle and the mass in which it has its line of travel. This paddle is frequently built into a gate, which is a multiplicity of paddles joined into a framework by members running more or less parallel to the shaft on which the paddle rotates. Again the paddles or gates may be assisted by baffles in the vessel. These baffles may be simply planes of deflection for the flowing mass of material, or may be so arranged as to dovetail, or mesh, into the rotating paddle. Again, the paddle may comprise a series of flights or shoes upon a chain or rope, and the agitation be produced by the traveling of this paddle in other than a rotating path. For an example of this latter case we have the ordinary button type conveyor when used as a mixer. Again, the paddle may consist of a spiral, as in the usual helical type of screw conveyor, or may have peculiar forms so as to give both a rotating and a grinding action, as in a dough mixer.

(*d*) The ship propeller. Although the ship propeller may be considered as a special case of the paddle, yet its development has been so nearly complete that it should be given a separate place. This is an ordinary ship propeller operated at a high speed, which is placed in a tank containing liquids

or gases, or mixtures thereof. This high-speed propeller may be used alone in the tank or preferably in connection with a draft tube or other baffling device, so as to insure a flow of material without the building up of so-called dead spaces or miniature "sargasso" seas. Again, the propeller may be inserted so as to have its shaft in a vertical direction through the top or the bottom of the tank, or it may be inserted on the sides through a stuffing box below the level of the liquid, and when thus inserted may be either at right angles to the center of the tank or at an angle oblique thereto, so as to produce tangential motion either with or without breaking up by baffles.

(*e*) Turbine type. These are an outgrowth of the propeller and may be considered a special case thereof. As, however, they have been highly developed and operate on a slightly different principle, their classification here as a separate method has been included. These turbine types consist merely of placing the rotor of a turbine on the end of the shaft instead of the propeller and having the turbine rotate within a guide ring. A special type of turbine propeller utilizes the principle of the impeller of a pump rather than, strictly speaking, a turbine.

(*f*) Gas agitation. Gases under pressure are frequently inserted in the bottom of a vessel where agitation is needed, and by their expansion and upward flow create currents. This method may be combined with any of the other methods of agitation indicated, and is particularly applicable where the gas used plays a prominent part in the reaction itself. The gas most used where agitation alone is desired without the chemical reaction is, of course, compressed air. It is not particularly applicable where the materials are liable to be carried off by the air, which must escape from the top of the tank after it has performed its useful function.

(*g*) Pumps. A method of agitation often used for some substances consists in drawing out of a large storage tank a liquid or gas through a centrifugal pump so designed as to produce an intimate mixture as the materials pass through the impeller of the pump. Frequently a small mixing chamber having baffles therein is placed on the pressure

side of the pump, so that in addition to the mixing obtained inside the pump casing itself there is a further mixing or agitation as the material passes over the baffles in the mixing chamber. Again, this mixing chamber may consist of a pump working in opposition to the first or primary pump, in which case, of course, the secondary or mixing pump must be of less power than the primary or forcing pump.

(*h*) Water falls agitation. This consists merely in having the material to be mixed taken to a height and allowed to fall along a channel having steps in it, so that as the liquid hits the first step it is mixed with the liquid falling.

(*i*) Spray agitation. In this case the liquid to be agitated is sprayed through a nozzle, either into a strong draft of air or through gas, at more or less right angles to the direction of the flow of the spray.

(*j*) Electro magnetic, in which case there is no moving part other than the material to be agitated, which is acted upon by a magnetic field so as to produce movement. This is used extensively in the inductive type of electric furnace and in certain electrolytic operations.

(*k*) Other types of agitation are possible, and are known to exist, but have not been included herein from a belief that their use is not extensive.

The particular type of agitator to be used in any case, of course, depends upon the exact results that are desired, and no general rule can be given which will apply to all cases. Most of the above types of agitators may not be an integral part of the containing vessel itself, but may be attached to a separate frame so that the agitator may be lowered into its position for an interval and then taken from that first tank to another tank to be agitated. When the size of the vessel itself is small, it may be brought underneath the agitator, as, for instance, was frequently done in melting TNT for pouring high-explosive shell.

Of course, many of the above types of agitators may be combined in the same vessel, and may be operated under such conditions as to give so-called selective agitation. We look forward expectantly to the extension of the author's method to determining the efficiency of these other types.

PRESIDENT HOWARD: I think you will find that the rate of stirring

with that type of stirrer is very largely a function of the diameter of the tank and agitator. For instance, in a vessel three inches in diameter seven revolutions per minute would give you very inefficient stirring. It is rather the rim speed of the liquid being stirred which counts, I think, but the rim speed necessary for good stirring probably increases somewhat but not directly with the diameter of the vessel.

MR. BADGER: Mr. Howard's idea is entirely reasonable and will be touched on when we have progressed further in this investigation.

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